JOURNAL OF

THE INSTITUTE OF PETROLEUM

FOUNDED 1913+INCORPORATED 1914

Vol. 39 APRIL 1953 No. 352

Contents

Sulphur Compounds in Petroleum
By S. F. Birch

Preparation and Properties of Dialkyl Di- and Poly-Sulphides
By S. F. Birch, T. V. Cullum, and R. A. Dean

The Isomeric Thiophthens and their Ethyl Homologues
By F. Challenger and B. Fishwick

The New Standard Method for the Measurement of Viscosity

Application of Paper Partition Chromatography to Petroleum Analysis
By E. Mariani

Abstracts Book Reviews Additions to Library

Published by the Institute of Petroleum
26 Portland Place, London, W.1
Telephone No.: LANgham 2250
Telegraphic Address: Instpetech, Westdo, London
Printed in Great Britain by Richard Clay and Company, Ltd., Bungay, Suffolk

Price 10s. 0d. Annual Subscription £4 14s. 6d. (Post Free)

COUNCIL, 1953–54

PRESIDENT

H. S. Gibson, C.B.E., M.A., M.I.Mech.E.

PAST-PRESIDENTS

Sir Andrew Agnew, C.B.E.
S. J. M. Auld, O.B.E., M.C., D.Sc.
T. Dewhurst, A.R.C.S.
A. E. Dunstan, D.Sc., F.R.I.C.
E. A. Evans, M.I.Mech.E., F.R.I.C.
F. H. Garner, O.B.E., Ph.D., F.R.I.C.
C. A. P. Southwell, C.B.E., M.C., B.Sc.

VICE-PRESIDENTS

E. B. Evans, M.Sc., Ph.D., F.R.I.C.
H. Hyams
J. A. Oriel, C.B.E., M.C., M.A., B.Sc., F.R.I.C.
H. E. F. Pracy, B.A., M.I.Chem.E.
R. B. Southall
G. H. Thornley, M.Sc.

MEMBERS OF COUNCIL

W. S. Ault, B.A.
V. Biske, B.Sc., LL.M., F.R.I.C.
C. D. Brewer, M.I.Mech.E.
E. J. Dunstan, M.Sc., M.I.Chem.E.
F. L. Garton, M.A., B.Sc.
A. J. Goodfellow, B.Sc., A.R.I.C.
A. C. Hartley, C.B.E., F.C.G.I., B.Sc. (Eng.), M.I.C.E., M.I.Mech.E.
E. LeQ. Herbert, B.Sc., F.R.I.C.
E. C. Masterson, B.Sc.
F. Morton, Ph.D., D.Sc., F.R.I.C.
J. S. Parker, M.A., B.Sc.
A. J. Ruthven-Murray, M.A., B.Sc.
D. L. Samuel, B.Sc., A.R.I.C.
G. H. Smith, Ph.D.
A. R. Stark, B.Sc., A.R.I.C.
E. J. Sturgess, B.Sc.
W. H. Thomas, A.R.S.M.
O. F. Thompson, O.B.E.
A. T. Wilford, B.Sc., F.R.I.C.
C. S. Windebank, B.Sc., M.S.

EX-OFFICIO

S. A. Berridge. Fawley Branch
A. W. Deller, D.F.C. London Branch
H. H. Ballard. Northern Branch
W. M. Stirling, A.H.-W.C., A.M.I.E.E. Scottish Branch
N. W. Grey. South-Eastern Branch
E. J. Horley. South Wales Branch

HONORARY SECRETARY: C. Chilvers, B.Sc., F.R.I.C.

HONORARY TREASURER: G. H. Coxon

GENERAL SECRETARY: D. A. Hough, A.I.A.C.

HONORARY EDITOR: F. H. Garner, O.B.E., Ph.D., F.R.I.C.

HONORARY ASSOCIATE EDITOR: E. B. Evans, M.Sc., Ph.D., F.R.I.C.

EDITOR: George Sell

HONORARY SECRETARIES OF BRANCHES

Fawley Branch: S. A. Berridge, c/o Esso Petroleum Co. Ltd., Fawley, Southampton.

London Branch: R. F. Leach, M.A., c/o Shell-Mex and B.P. Ltd., Shell-Mex House, Strand, London, W.C.2.

Northern Branch: G. M. Davies, c/o Esso Petroleum Co. Ltd., Mode Wheel Installation, Trafford Wharf Road, Manchester 17.

Persian Gulf Branch: G. A. Hogg, B.A., c/o Kuwait Oil Co. Ltd., Kuwait, Persian Gulf.

Scottish Branch: W. M. Stirling, A.H.-W.C., A.M.I.E.E., Scottish Oils Ltd., Middleton Hall, Uphall, Broxburn, W. Lothian.

South-Eastern Branch: F. A. Maliphant, c/o Anglo-Iranian Oil Co. Ltd., Kent Oil Refinery, Isle of Grain.

South Wales Branch: E. J. Horley, National Oil Refineries Ltd., Llandarcy, Glam.

Stanlow Branch: V. Biske, B.Sc., LL.M., F.R.I.C., Lobitos Oilfields Ltd., The Refinery, Ellesmere Port, Cheshire.

Trinidad Branch: H. C. Costelloe, c/o Apex (Trinidad) Oilfields Ltd., Siparia P.O., Trinidad, B.W.I.

THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute was held at 26 Portland Place, London, W.1, on 11 November 1952; the President, H. S. Gibson, C.B.E., was in the Chair.

THE PRESIDENT: It is my pleasant duty to introduce Dr S. F. Birch, who has been interested in the field of research on sulphur compounds in petroleum for many years, in fact, since he first joined the old Anglo-Persian Oil Company.

Not only has Dr Birch been engaged in studying sulphur compounds in petroleum, but he has carried out a great deal of research in organic chemistry in general, and in hydrocarbon reactions in particular. You will probably remember that he has contributed a great deal to the process of alkylation, which was known in its early days as the "acid condensation" or "alkanation" process. He also contributed to super-fractionation.

DR BIRCH then presented the following paper.

SULPHUR COMPOUNDS IN PETROLEUM

By S. F. BIRCH*

THE majority of crude oils contain sulphur in amounts up to 5 per cent, so that the problems of desulphurization and sweetening are very general. Early refining processes worked out for the distillates by purely *ad hoc* methods consisted mainly of treatment with such reagents as aqueous caustic soda, sulphuric acid, sodium plumbite, or absorbent materials such as clay or bauxite. Later hypochlorites were employed for desulphurizing and sweetening lighter distillates, while for the heavier fractions solvent extraction with sulphur dioxide was employed. The introduction of cracking rendered the problem more difficult owing to the presence of olefins in the naphthas produced.

These refining methods were on the whole costly and wasteful, and the necessity for disposing of the spent refining agents constituted a problem of its own.

Since that time the petroleum industry has progressed far. Some of the earliest refining agents still remain in use, but are applied far more scientifically and economically. The main change has, however, been towards catalytic processes and physical methods.

While these advances have been due in some measure to an understanding of the reactions and physical processes involved, many of them have still been the result of *ad hoc* investigations. A better knowledge of the sulphur compounds present in the distillates, particularly in the low-boiling ranges, has, however, proved extremely helpful in developing and

* The Anglo-Iranian Oil Co. Ltd., Research Station, Sunbury-on-Thames, Middlesex.

improving refining processes. Prior to 1920 a few chemists had interested themselves in the sulphur bodies in petroleum, but it was not until this time that the petroleum industry began to appreciate the value of such investigations. From then onwards a considerable amount of research, both of a fundamental and applied nature, has been carried out in this field, which, in the States, has culminated in the A.P.I. Project 48. In spite of the very extensive literature that has been built up on the subject, much yet remains to be learned, especially with regard to the sulphur bodies in the higher-boiling distillates.

No two crudes are exactly alike in composition or behaviour on processing. This is well illustrated by the work of Smith and Ball and their collaborators,[1] who have investigated the nature of the sulphur bodies in the straight-run naphtha to 250° C both under atmospheric and reduced pressure from a wide variety of crude oils, including a number from the United States and the Middle East. Their results show that the types of sulphur compounds vary from one crude to another and demonstrate the effect of distillation conditions. They also emphasize the limitations of the methods of analysis available, since from 17 to 80 per cent of the sulphur present could not be classified. The method employed enabled an estimate of the sulphides, mercaptans, and disulphides to be obtained as well as of hydrogen sulphide and elemental sulphur, but was incapable of differentiating between mercaptan types or open-chain and cyclic sulphides.

The development of a reliable type analysis for sulphur bodies is rendered difficult by lack of knowledge of the various forms in which sulphur may be present in distillates. The number of individual types is not large, but there is considerable variation in each of these owing to the influence of the attached alkyl groups. Mercaptans may be primary, secondary, or tertiary, and since their behaviour towards, for example, oxidizing agents depends to some extent upon their type, it is of interest to be able to distinguish between one class and another.

Very few petroleum distillates, even in the light naphtha range, have been exhaustively examined, and until this has been done it is obvious that a satisfactory method of type analysis cannot be developed. Of the naphthas which have been investigated some of those from Middle East crude oils have probably been most fully studied.

Sulphur Compounds in Middle East Naphthas

The sulphur bodies present in lighter fractions from certain Iranian crude oils have for some time been under investigation, as a result of which a number of the individual compounds present have been isolated. The greater part of this work has been carried out on sulphur bodies recovered from spent treating agents, the refining processes providing convenient methods for their concentration. The possibility that the compounds recovered might not be those present in the original distillate was appreciated, but it was anticipated that they would provide a clue to the identity of the parent substance.

From the caustic soda wash from a light Naft-Khaneh distillate a mixture of mercaptans was obtained from which the mercaptans shown in Table I were separated by fractionation. The same mercaptans, together

with methyl mercaptan, were also isolated from soda used to treat a straight-run Agha Jari distillate. Some of these mercaptans had previously been isolated from the soda washings from a Masjid-i-Sulaiman distillate.[2]

TABLE I

	Boiling point, °C at 760 mm
Methyl mercaptan	6·5
Ethyl mercaptan	35·04
*iso*Propyl mercaptan	52·60
n-Propyl mercaptan	67·82
sec-Butyl mercaptan	85·15
*iso*Butyl mercaptan	88·72
n-Butyl mercaptan	98·58

Higher-boiling mercaptans were also present from which a fraction consisting of mixed pentanethiols was obtained. Attempts to separate and identify these were, however, unsuccessful.

An examination of the neutral sulphur compounds recovered from acid used to treat a straight-run Iranian naphtha of similar boiling range to that from which the mercaptans were isolated, was first made by Thierry.[3] This naphtha was derived from a Masjid-i-Sulaiman crude. Later a similar investigation was made of the sulphur bodies from an acid sludge produced in refining an SO_2-extract of a light straight-run naphtha of Iranian origin.[4, 5] The compounds isolated were found to be mainly open-chain and cyclic sulphides, the remainder consisting of dialkyl disulphides formed by oxidation from mercaptans present in the extract. Table II shows the sulphides which have been isolated from these acid sludges.

TABLE II

Sulphides Isolated from Acid Sludges from Light Naphthas

Open-chain Sulphides.
Methylethyl sulphide.[3]
Ethyl-*n*-propyl sulphide.[5]
*iso*Propyl-*n*-propyl sulphide.[5]

Cyclic Sulphides.[3, 4]
Thia*cyclo*pentane.
2-Methylthia*cyclo*pentane.
3-Methylthia*cyclo*pentane.
Thia*cyclo*hexane.

These cyclic sulphides have all been isolated previously from straight-run petroleum distillates by other workers.[6–9] The separation of the individual cyclic sulphides was effected by fractionation, followed by selective adsorption on silica gel. Since reliable data on the physical properties of both open-chain and cyclic sulphides were required for this investigation, and none were available, several of these compounds were prepared synthetically in a high state of purity and their physical properties determined.[10, 11] These are shown in Tables III and IV.

More recently this investigation has been extended to an acid sludge from the treatment of an Agha Jari kerosine SO_2-extract.[12] In this range the isolation of individual compounds has proved difficult and sometimes impossible. Even after fractionation through efficient columns, the plateaux obtained consisted of several closely boiling compounds. How-

ever, fractional extraction of narrow cuts with aqueous mercuric acetate [13] enabled further separation to be effected by providing a means for separating open-chain and cyclic sulphides as well as thiophenes which were found to be present. The latter have been mentioned in the literature as components of straight-run naphtha, but no reliable supporting evidence has been given; this therefore appears to be the first occasion that their presence has been definitely established. It is interesting to note that the thiophenes identified were either tri- or tetra-substituted derivatives (Table V). The former reacted with mercuric acetate to yield stable oil-soluble mercuriacetates from which the thiophenes were regenerated by heating with hydrochloric acid. Tetra-substituted thiophenes are incapable of reaction, and were left unattacked.

TABLE III

Compound	Physical properties of the dialkyl sulphides				
	Formula	Boiling point at 760 mm Hg, ° C	Refractive index, n_D^{20}	Melting point for zero impurity, ° C	Purity, mole %
Dimethyl sulphide	$CH_3{\cdot}S{\cdot}CH_3$	37·3	1·4353	− 98·25	99·95
Methylethyl sulphide	$CH_3{\cdot}S{\cdot}C_2H_5$	66·6	1·4403	−105·91	99·90
Methyl*iso*propyl sulphide	$CH_3{\cdot}S{\cdot}C_3H_7$	84·8	1·4392	−101·48	99·8
Diethyl sulphide	$C_2H_5{\cdot}S{\cdot}C_2H_5$	92·0	1·4427	−103·91	99·8
Methyl-*n*-propyl sulphide	$CH_3{\cdot}S{\cdot}C_3H_7$	95·6	1·4442	−112·98	99·96
Ethyl*iso*propyl sulphide	$C_2H_5{\cdot}S{\cdot}C_3H_7$	107·3	1·4407	−122·19	99·85
Ethyl-*n*-propyl sulphide	$C_2H_5{\cdot}S{\cdot}C_3H_7$	118·5	1·4461	−117·04	99·8
Di*iso*propyl sulphide	$C_3H_7{\cdot}S{\cdot}C_3H_7$	119·8	1·4388	− 78·08	99·93
Ethyl-*tert*-butyl sulphide	$C_2H_5{\cdot}S{\cdot}C_4H_9$	120·4	1·4417	− 88·95	99·97
Propyl*iso*propyl sulphide	$C_3H_7{\cdot}S{\cdot}C_3H_7$	132·1	1·4440	—	—
Ethyl-*sec*-butyl sulphide	$C_2H_5{\cdot}S{\cdot}C_4H_9$	133·6	1·4477	—	—
Ethyl *iso*butyl sulphide	$C_2H_5{\cdot}S{\cdot}C_4H_9$	134·2	1·4450	—	—
Di-*n*-propyl sulphide	$C_3H_7{\cdot}S{\cdot}C_3H_7$	142·8	1·4487	—	—
Ethyl-*n*-butyl sulphide	$C_2H_5{\cdot}S{\cdot}C_4H_9$	144·2	1·4491	− 95·13	99·8

TABLE IV

Physical Properties of the Monocyclic Sulphides

Compounds	Boiling point, ° C	Refractive index, n_D^{20}	Melting point for zero impurity, ° C	Purity, mole %
Thia*cyclo*pentane	121·2/760 mm	1·5047	− 96·06	99·7
2-Methylthia*cyclo*pentane	132·4/760 mm	1·4909	−100·71	99·75
3-Methylthia*cyclo*pentane	138·2/760 mm	1·4924	− 81·16	99·7
cis-2 : 5-Dimethylthia*cyclo*pentane	60·0/ 45 mm	1·4799	− 89·4	99·3
trans-2 : 5-Dimethylthia*cyclo*pentane	58·0/ 44 mm	1·4776	− 76·35	99·3
Thia*cyclo*hexane	141·6/760 mm	1·5067	+ 19·07	99·90
2-Methylthia*cyclo*hexane	55·0/ 26 mm	1·4905	− 58·14	99·2
3-Methylthia*cyclo*hexane	157·9/760 mm	1·4922	− 60·17	99·8
4-Methylthia*cyclo*hexane	54·0/ 22 mm	1·4923	− 28·11	99·8

The compounds extracted by means of cold aqueous mercuric acetate solution were found to be sulphides, of which a few per cent were open-chain compounds; these were not further investigated. The bulk, however, consisted of mono- and bi-cyclic sulphides. The identification of the cyclic sulphides was largely based on physical properties, the melting points of their mercurichlorides, and upon the spectroscopic analysis of the

TABLE V

Thiophenes Present in Acid Sludge from Kerosine Extract

Compound	Boiling point, ° C/760 mm (approx)
2 : 3 : 4-Trimethylthiophene	176
2 : 3-Dimethyl-4-ethylthiophene . . .	193
2 : 3 : 4 : 5-Tetramethylthiophene . . .	193–196
2 : 3 : 4-Trimethyl-5-ethylthiophene . .	205–206

hydrocarbons obtained on treatment with Raney nickel. This method of identification is dependent upon the desulphurizing action of the metal [14] when a solution of the sulphur compound is heated in the presence of a very large excess of Raney nickel, the sulphur being eliminated and replaced by hydrogen. Open-chain sulphides give two hydrocarbon molecules corresponding with the original alkyl groups, while those in which the sulphur is attached to the two ends of the carbon chain, as in a cyclic sulphide, give only one hydrocarbon

$$R_1SR_2 + (Ni)H_2 \longrightarrow R_1H + R_2H + NiS$$

$$(H_2C)_n\begin{matrix}CH_2\\ \\ CH_2\end{matrix}S + (Ni)H_2 \longrightarrow (H_2C)_n\begin{matrix}CH_3\\ \\ CH_3\end{matrix} + NiS$$

The resultant hydrocarbon or mixture of hydrocarbons can, if necessary, be fractionated and the components identified spectroscopically. This useful technique can be applied to comparatively small quantities of material, a micro-column of the type described by Bower and Cooke [15] being employed when necessary to fractionate the hydrocarbons. The cyclic sulphides identified in this way together with those probably present are shown in Table VI.

On treatment with Raney nickel, several of the fractions in which individual compounds appeared to have been concentrated yielded substituted *cyclo*pentanes and *cyclo*hexanes. From boiling range and higher refractive indices of these fractions, it was concluded that these had been formed from bicyclic sulphides containing fused five- and six-membered fully hydrogenated rings. The presence of such compounds in our material is in line with the work of Brown and Meyerson, who, from a mass spectrometric analysis of higher-boiling sulphides of West Texas origin, concluded that bicyclic sulphides were present.[16] Although some of the naphthenes may have been formed from alkyl *cyclo*-alkyl sulphides (the presence or absence of which has not yet been established), the high refractive index

of the fractions of the original sulphur compounds indicated the presence of the bicyclic compounds, since the simple alkyl *cyclo*-alkyl sulphides have refractive indices (n_D^{20}) of the order of 1·49, *e.g.*, methyl*cyclo*hexylsulphide (1·4946). Complete identification of these interesting bicyclic compounds was not easy, as the parent sulphur compound could rarely be obtained in a sufficiently pure state, with the result that the hydrocarbons obtained by

TABLE VI

Cyclic Sulphides Present in Acid Sludge from Kerosine Extract

Compound	Boiling point, ° C/760 mm
2-Methylthia*cyclo*pentane *	132
3-Methylthia*cyclo*pentane *	137
Thia*cyclo*hexane *	141
2 : 4-Dimethylthia*cyclo*pentane	148
2 : 3-Dimethylthia*cyclo*pentane	148
2-Methylthia*cyclo*hexane	153
2-Ethylthia*cyclo*pentane	155–159
3-Methylthia*cyclo*hexane	155–159
4-Methylthia*cyclo*hexane	155–159
2 : 3 : 5-Trimethylthia*cyclo*pentane	155–159
3 : 4-Dimethylthia*cyclo*hexane and/or 2 : 3 : 4-Trimethylthia*cyclo*pentane	164
2 : 6-Dimethylthia*cyclo*hexane and/or 2-Ethyl-5-methylthia*cyclo*pentane	164
3-Methyl-4-ethylthia*cyclo*pentane and/or 3-Isopropylthia*cyclo*pentane	180
2 : 3-Dimethyl-5-ethylthia*cyclo*pentane and/or 2 : 4-Diethylthia*cyclo*pentane and/or 2 : 3 : 6-Trimethylthia*cyclo*hexane	180
2 : 5-Dimethyl-3-ethylthia*cyclo*pentane and/or 2 : 3-Diethylthia*cyclo*pentane	180

* Previously isolated from "benzine extract" acid sludge.

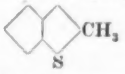
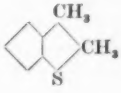
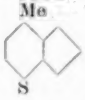
desulphurization were mixtures of naphthenes difficult to analyse. Identification of the latter was rendered more difficult by the presence of geometrical isomers, few of which, particularly di-substituted *cyclo*pentanes, are available for comparison. Yet a further complication was the possibility that during desulphurization ring expansion, which almost invariably takes place when the *cyclo*pentylmethyl radical is involved,[17] had occurred :

Desulphurization of several sulphur bodies, *i.e.*, di-*cyclo*pentylmethyl sulphide, *cis*- and *trans*-2-thiadecalin, provided, however, no evidence that isomerization either involving ring expansion or *cis*/*trans* re-arrangement does in fact occur under the conditions employed.

In Table VII the hydrocarbons obtained from a number of the fractions and the bicyclic sulphides from which they were probably derived are shown. It is interesting to note that several of these appear to be thia-[0 : 3 : 3]-bi*cyclo*-octane derivatives consisting of two five-membered rings.[8,16] This is in line with the generally held view that many of the higher petroleum hydrocarbons contain two or more *cyclo*pentane rings.[18]

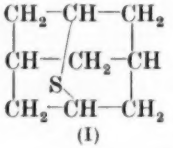
TABLE VII

Bicyclic Sulphides from Acid Sludge from Kerosine Extract

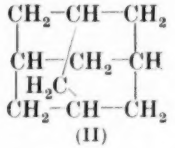
Boiling point of fraction, °C/760 mm	Naphthene obtained on desulphurization	Probable bicyclic sulphide
191	Ethyl*cyclo*pentane	2-Thia[0 : 3 : 3]bi*cyclo*-octane
193–196	*n*-Propyl*cyclo*pentane	3-Methyl-2-thia[0 : 3 : 3]bi*cyclo*-octane *  6-Thia[0 : 3 : 4]bi*cyclo*nonane *
202	*iso*Propyl*cyclo*pentane	4-Methyl-2-thia[0 : 3 : 3]bi*cyclo*-octane
208	Ethyl*cyclo*hexane	2-Thia[0 : 3 : 4]bi*cyclo*nonane
209–210	*sec*-Butyl*cyclo*pentane	3 : 4-Dimethyl-2-thia[0 : 3 : 3]bi*cyclo*-octane  AND/OR 4-Ethyl-2-thia[0 : 3 : 3]bi*cyclo*-octane * AND/OR 9-Methyl-6-thia[0 : 3 : 4]bi*cyclo*nonane * 

* Alternative structures yielding same naphthene.

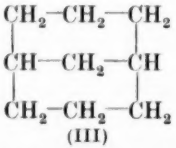
During the fractionation of the above sulphides, it was observed that a high-melting white solid collected in the column-head assembly. More of this solid was obtained when the fraction boiling at 225° C was chilled. After purification by crystallization, it gave an analysis corresponding with $C_9H_{14}S$, and formed both a mercurichloride and a sulphone. The structure of this interesting substance, the first solid sulphur compound isolated from petroleum, has not yet been absolutely established. There is, however, little doubt that it is the tricyclic sulphide (I) corresponding to the hydrocarbon adamantane (II) isolated by Landa and Macháček from a Hodonin, Yugo-Slavia, naphtha [19] and later synthesized by Prelog and Seiwerth.[20] On desulphurization with Raney nickel it gave [1 : 3 : 3]bi-*cyclo*nonane (III),[21] to be expected from the thia-adamantane structure depicted :—



(I)



(II)



(III)

Even before their presence had been definitely established, the possibility that bicyclic sulphides would be encountered in distillates boiling above the gasoline range had been considered. Few compounds of this type have been previously described, and these have contained an aromatic nucleus. As little reliable physical data were available for any of these compounds and their spectra had not been determined, the synthesis of these and a number of typical bicyclic sulphides containing fully hydrogenated fused five- and six-membered rings was undertaken. The latter were all compounds of type A or B in which a thia*cyclo*pentane or thia*cyclo*hexane ring is fused to a *cyclo*hexane ring.

Type A.

Type B.

This work, which is still in progress, has been rendered difficult by the fully hydrogenated compounds existing in *cis* and *trans* forms. This has necessitated employing a method of synthesis in which all possibility of isomerization is avoided. As a check on this, the purity of intermediates involved in the syntheses has been determined at each stage and, wherever possible, derivatives prepared for comparison with known substances. In

Table VIII the bicyclic derivatives so far prepared are shown with their more important physical properties.[22] Knowledge of the refractive indices and behaviour of these sulphides towards such reagents as aqueous mercuric acetate solution [13] materially assisted the investigation into the composition

TABLE VIII

Physical Properties of Bicyclic Sulphides

Compound	Formula	Boiling point, °C/760 mm Hg (extrapolated)	Refractive index, n_D^{20}	Melting point for zero impurity, °C	Purity, mole %
		Aromatic Bicyclic Sulphides			
1-Thiaindane		235·58 *	1·6212	− 3·23	99·7
2-Thiaindane		241·5 *	1·6039 (n_D^{25})	+25·12	99·43
1-Thiatetralin		254·0 *	1·6145	−14·95	99·82
2-Thiatetralin		264·7 *	1·6076	+0·789	99·89
		Naphthenic Bicyclic Sulphides			
cis-3-Thia[0 : 3 : 4]bicyclononane (*cis*-2-Thiahydrindane)		108·5/21 mm	1·5313	—	—
trans-3-Thia[0 : 3 : 4]bicyclononane (*trans*-2-Thiahydrindane)		105/20 mm	1·5248	+ 4·28	99·87
cis-2-Thia[0 : 4 : 4]bicyclodecane (*cis*-1-Thiadecalin)		†	—	—	—
trans-2-Thia[0 : 4 : 4]bicyclodecane (*trans*-1-Thiadecalin)		80–82/2·0 mm	1·5210	−23·5 approx	—
cis-3-Thia[0 : 4 : 4]bicyclodecane (*cis*-2-Thiadecalin)		246·0 *	1·5335	− 3·614	99·87
trans-3-Thia[0 : 4 : 4]bicyclodecane (*trans*-2-thiadecalin)		115·5–116·5/20 mm	1·5215	+ 9·383	99·89

* Boiling points determined by a Swietoslawski apparatus.
† Compound in course of preparation.

of the kerosine extract sulphur bodies. The probability that bicyclic sulphides are present in which a *cyclo*pentane ring is fused to a thia*cyclo*pentane or thia*cyclo*hexane ring,[16] and that ring expansion occurs during their desulphurization, makes it highly desirable that compounds of this type should be synthesized and examined. One such compound, 2-thia-[0 : 3 : 3]-bi*cyclo*-octane, has already been prepared by us in small amounts.

The difficulties which have been experienced in examining the sulphur bodies of the kerosine range are likely to prove far greater in the next higher boiling range. Even the sulphur bodies from the back end of the kerosine extract have so far proved inseparable. Some knowledge of the general types of compounds present in the higher fractions would, however, be of interest, especially when it is appreciated that, for example, in the gas oil

range a sulphur content of 1 per cent is equivalent (assuming one sulphur atom per molecule) to some 7 to 10 per cent of sulphur-containing compounds.

Sulphur Bodies in Crude Oil

The form in which sulphur is present in crude oils before distillation is of considerable interest both to the refiner and to the geologist, since knowledge on this point might throw light on the formation of petroleum.

There can be little doubt that petroleum is biological, and probably largely vegetable, in origin. Strong evidence for the former is provided by the work of Treibs,[23] who has demonstrated the presence of porphryins in a large number of crude oils. Decomposition under anærobic conditions with bacterial assistance no doubt resulted in the slow conversion of carbohydrates and similar constituents into hydrocarbons, during this process other elements such as oxygen, nitrogen, etc., being mostly eliminated in one way or another. While the possibility that sulphur compounds present in the crude oils may have been formed during this period cannot be excluded, it seems doubtful whether sufficient sulphur would have been present at this stage to account for the combined sulphur found in the majority of sulphur-containing crudes. An alternative is that the sulphur was introduced at a somewhat later stage from the sulphates of surrounding rock formations through the agency of bacteria. That under anærobic conditions the latter are capable of oxidizing hydrocarbons to carbon dioxide, using sulphate-oxygen and producing hydrogen sulphide as by-product, has been demonstrated by the work of Zobell and Butler. The action of this hydrogen sulphide upon oxygenated and possibly even nitrogen-containing bodies remaining in the oil may explain the presence of the combined sulphur in those crude oils in which it is found.

The presence of cyclic sulphides found in petroleum distillates in itself presents an interesting problem. Few naturally occurring substances are known in which the thia*cyclo*-pentane or -hexane structure is to be found.* Thiophenes are present in coal-tar and shale distillates, but these have almost certainly been formed during the higher temperatures in the retorting operation.[24] How then have cyclic sulphides been formed in petroleum? Whether cyclic sulphides are normal components of petroleum distillates has not been determined. They have, however, been detected in the distillates from crude oils of world-wide origin [6-9, 25, 26] besides those mentioned above from the Middle East.

Cyclic sulphides may be products of some decomposition reaction, although the apparent absence of other degradation products renders this unlikely. Nor does it seem very probable that they have been formed by the hydrogenation of thiophenes (resulting from the action of sulphur on paraffins [27, 28] or hydrogen sulphide on diolefins) [29] followed, in the case of thia*cyclo*hexane derivatives, by isomerization. While the catalytic-hydrogenation of thiophenes has been effected by Moldavskii and Prokonchuk [30] and by Mozingo,[31] we have been unable to convert the methylthia*cyclo*pentanes into thia*cyclo*hexane or *vice versa* by isomerization with

* α-Terthienyl has been identified in the common African marigold *Tagetas erecta*, L., by L. Zechmeister and J. W. Sease (*J. Amer. chem. Soc.*, 1947, **69**, 273). Biotin possesses a modified thia*cyclo*pentane structure.

the powerful catalyst, aluminium chloride, so effective with the corresponding hydrocarbon conversion. None of these compounds was isomerized when heated with the catalyst at 100° C for 60 hr.

While neither the thia*cyclo*pentane nor thia*cyclo*hexane structure occurs in natural products to any extent worth considering, compounds containing the analogous oxygen and nitrogen structure abound. Furan rings occur in many carbohydrates, furfural being obtained by the acid hydrolysis of pentosans from corn cobs, oat husks, etc., while sylvan (2-methyl-furan) is found in the fore-runnings from the oil of the *pinus sylvestris* and beechwood tars. Dimethylfurans have been found in other similar distillates. The pyran ring is also found in carbohydrates, plant pigments, and so on. Furthermore, the dehydration–isomerization of tetrahydrofurfuryl alcohol to dihydropyran is readily effected. The corresponding nitrogen compounds, the pyrrols and pyridines, are also commonly met with in natural products. The porphyrins, isolated by Treibs from various crude oils, contain the pyrrol ring as part of their structure, while both pyridine and quinoline derivatives have been identified in Californian oils by Lochte.[32]

It is interesting to explore the possibility that the petroleum cyclic sulphides may have originated from such substances by the action of hydrogen sulphide. Yur'ev and his co-workers [33] have shown that at 400° to 450° C in the presence of an alumina catalyst, hydrogen sulphide will bring about the replacement of the oxygen of the tetrahydrofuran and pyran rings by sulphur :—

Tetrahydrofurfuryl alcohol undergoes ring expansion and a mixture of thia*cyclo*hexene-2 and thia*cyclo*hexane is obtained.[34]

Yur'ev and Bugorkova [35] have also found that under similar conditions pyrrolidine is converted into thia*cyclo*pentane, although not nearly so readily :—

The temperatures of 400° to 450° C under which these reactions have been found to occur are appreciably higher than those to which petroleum can normally have been subjected; according to Treibs the temperature in petroleum formation cannot have exceeded 240° C, at which temperature the porphyrin–carboxylic acids present in some typical crude oils would have undergone rapid decarboxylation. The question then arises whether these reactions can reasonably be postulated to have occurred at lower temperatures in the very long times available. An attempt [36] was made to derive the free energy change and equilibrium constant for the reaction of tetrahydrofuran and hydrogen sulphide to give thia*cyclo*pentane and water and to find how the equilibrium changes with temperature. Thermo-

dynamic data for the cyclic compounds are lacking, but it is considered that the analogous reaction of dimethyl ether to dimethyl sulphide is sufficiently similar to serve as a guide, the bond changes being exactly similar in the two cases. For this reaction :—

$$CH_3OCH_3 + H_2S = CH_3SCH_3 + H_2O$$

it is found that throughout the relevant temperature range there is a large negative free energy change for the reaction going from left to right, so that the equilibrium in this reaction is consistently far over to the right; indeed, the calculation shows that as the temperature is lowered from 450° C the equilibrium moves increasingly in favour of dimethyl sulphide. It appears therefore that the reaction of tetrahydrofuran to thia*cyclo*pentane continues to be thermodynamically feasible well within the temperature limits set by Treibs, and that in presence of a catalyst the reaction could occur given sufficient time. As an example, if it is assumed that the reaction has a temperature coefficient of 2 per 10° C then an extent of reaction which occurs in 1 hr at 400° C will take about 100 years at 200° C; this is a very short period compared with that which has been available in oilfields.

As an alternative to alumina the sulphactive metallic sulphides, described by Furlow, Lazier, and Signaigo [37] for the conversion of ketones and aldehydes to mercaptans were investigated. This reaction takes place in the presence of sulphur or hydrogen sulphide and a cobalt sulphide catalyst at 150° to 200° C and 2000 p.s.i. of hydrogen. It was found, however,[34] that while under these conditions tetrahydrofuran reacts readily to give thia*cyclo*pentane and intermediate products such as butane-1 : 4-thioglycol and dithiol, neither dihydro- nor tetra-hydropyran gave thia*cyclo*hexane, although the former did give polymeric material. Furthermore, attempts to convert sugars containing furanose and pyranose rings into cyclic sulphides were equally unsuccessful. Other metallic sulphides (iron, nickel) were tried with similar lack of success.

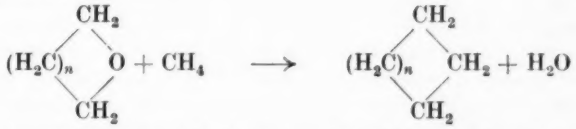
Thiophenes and Thia-adamantane

There is no way of determining whether the thiophenes identified in Agha Jari distillates have been formed directly from the corresponding furans or pyrrolidine and hydrogen sulphide [38] or by secondary reactions, such as the dehydrogenation of thia*cyclo*pentanes. Previously they have been found only in materials which have been heated to a relatively high temperature,* 600° C and above (which would exclude crude oils), or in the presence of catalysts, *i.e.*, catalytically cracked products. Since Friedmann [39] has shown that thia*cyclo*pentane is dehydrogenated by sulphur at 160° C to give thiophene and hydrogen sulphide, it is possible that the thiophenes identified in the Agha Jari kerosine may have been produced in this way from the corresponding thia*cyclo*pentanes.

The presence of adamantane and thia-adamantane in petroleum naphthas is not readily explained. That both the sulphide and structurally related hydrocarbon of such unusual structure should both be found is unlikely to be entirely coincidental, and this raises the question as to whether hydrocarbons structurally related to all the cyclic and open-chain sulphides found are present in petroleum distillates. With adamantane and its

* See footnote on p. 194.

thia-analogue, a common parent substance seems probable, but how in the former a sulphur has been introduced and in the other a methylene group in the same position is not easy to picture, unless some seemingly unlikely reaction is postulated between methane and an oxygenated body similar to that suggested for the formation of the cyclic sulphides through the agency of hydrogen sulphide :—



From thermodynamic data it is concluded [36] that such a reaction is theoretically feasible, particularly at lower temperatures. Whether bacteria are able to bring about this conversion either directly or indirectly is possibly worth exploring.

Polysulphides

The sulphur in distillates from some crude oils is almost entirely in the form of mercaptans or disulphides.[1] Whether disulphides are actually present in these crude oils or have been formed from mercaptans in some way is not clear, although the former seems the more probable. With such crude oils appreciable quantities of hydrogen sulphide and often sulphur are formed during distillation. This behaviour is consistent either with the presence of a thermally unstable sulphur compound decomposing during distillation or reactions of sulphur with hydrocarbons which commence only when a certain temperature has been reached. Evidence in support of this is that when distillation is carried out at reduced pressure, decomposition sets in much later and is determined by still-pot temperatures. The sulphur contents of fractions obtained when Agha Jari crude oil was distilled at atmospheric and reduced pressure (0·05 mm) are given in Table IX.[40]

Table IX

Fraction no.	Per cent on crude *	Atmospheric pressure		Reduced pressure	
		% S	50% point of fraction,† °C	% S	50% point of fraction,† °C
1	0 –12·7	0·066	97	0·043	96
2	12·7–19·5	0·127	156	0·082	146
3	19·5–27·7	0·221	185	0·141	189
4	27·7–34·3	0·335	223	0·371	238
5	34·3–54·3	0·964	299	1·02	300
6	54·3–64·9	1·68	408	1·67	407
	Residue				

* Sulphur content 1·42 per cent. † ASTM distillation.

In the earlier fractions distillation under reduced pressure gave fractions of lower sulphur content, but in the fourth and fifth fractions this is reversed, while the sulphur contents of the final distillates are identical. That this unexpected behaviour was due to the decomposition of a thermally

unstable substance (or the interaction of sulphur compounds and hydrocarbons) was indicated by the increase in mercaptan content of Fractions 3 and 4 obtained at reduced pressure on redistillation under ASTM conditions. Unless, therefore, the crude oil reaches a temperature of the order of 200° to 250° C little decomposition occurs. Obviously this temperature is reached much earlier in the atmospheric than in the reduced pressure distillates. Similar results have been reported by Ball, Smith, *et al* for a crude oil from Wasson, Texas.[41]

This behaviour of certain crude oils on distillation is consistent with the presence of elemental sulphur or unstable sulphur-containing substances, possibly alkyl polysulphides. This latter possibility prompted us to investigate the formation and general chemical and physical properties of some of these compounds.

Polysulphides are readily formed by the action of sulphur on mercaptans or mercaptides. With mercaptans, reaction is very slow in the cold, if indeed it occurs at all; it proceeds rapidly in the presence of secondary bases,[42] and is then accompanied by considerable evolution of heat. Even in the absence of catalysts reaction on heating is rapid, the product consisting of a mixture of the disulphide and polysulphides. Mercaptides in the presence of a suitable solvent, *i.e.*, which contains water for the alkali metal mercaptides and hydrocarbons for the heavy metal derivatives (*i.e.*, lead and mercury), react with great readiness at ordinary temperatures, while at higher temperatures the reaction proceeds even more rapidly.[43] Polysulphide formation is dependent upon reaction conditions, especially the relative proportions of the reactants; the main product is normally the disulphide. Elemental sulphur is not essential for these reactions, alkali metal, alkaline earth, and even higher dialkyl polysulphides reacting similarly. The ease with which mercaptans and sulphur react in aqueous solution explains the formation of polysulphides during the removal of hydrogen sulphide from light distillates by soda washing when insufficient care is taken to exclude air. Polysulphides are almost invariably formed in plumbite treatment when elemental sulphur or sodium polysulphides are used, unless conditions are especially chosen to avoid their formation.

Polysulphides are also formed by the action of sulphur on disulphides but not on monosulphides. This reaction takes place on heating, and is catalysed by secondary amines.[44] As a preparative method it is better suited to the comparatively stable *tert*-butyl derivative than the corresponding normal derivatives, thus it provides a convenient method for producing di-*tert*-butyl trisulphide from the corresponding disulphide.[45] Higher polysulphides are formed in this reaction, but no individual compounds appear to have been isolated.

The method by which the lengthening of the sulphur chain takes place in reactions of this kind is not clear, but dissociation of the disulphide into RS· radicals is a probable first step.[44] Direct addition of these to sulphur molecules would presumably lead to the formation of polysulphides containing up to ten sulphur atoms in a chain which would break down to give the more stable lower compounds. Measurements of the dipole moments [46] indicate that the sulphur chain in polysulphides is linear and not branched, which is supported by the formation of a urea adduct by di-*n*-butyl tetrasulphide.[44]

Although it has been claimed that penta- and hexa-sulphides have been obtained,[47, 48] it has not been possible to repeat this work nor to obtain higher polysulphides than the tetra- in a pure form by any means tried. The marked effect upon the lead response observed with some plumbite treated naphthas, coupled with the relatively small amounts of polysulphides responsible, suggests that some of the latter may have sulphur chains of well over four.

Individual polysulphides can be prepared in the laboratory by a number of methods, but these have no bearing upon their formation in petroleum or petroleum distillates. By such methods it has, however, been possible to prepare several polysulphides in a reasonable state of purity for examination. Table X gives a list of the polysulphides synthesized, together with their chief physical properties.[44]

Polysulphides in general are not very stable substances, the higher members tending to decompose spontaneously, for which reason they are not easily purified. Stability is determined by the groups attached to the sulphur chain and by the length of the latter. Primary alkyl derivatives are the least stable, and stability increases in the order primary < secondary < tertiary. Phenyl compounds appear to be somewhat less stable than primary alkyl derivatives. Increased stability resulting from alkyl groups is reflected in the stability of the tetrasulphides, the di-*tert*-butyl compound being comparatively stable, whereas it was not found possible to distil the corresponding dimethyl or diethyl derivatives without decomposition.

TABLE X

Physical Constants of the Polysulphides

	Dimethyl trisulphide	Diethyl trisulphide	Di-*n*-butyl trisulphide	Di-*tert*-butyl trisulphide	Di-*tert*-butyl tetrasulphide
Freezing point for zero impurity, ° C	−68·05	−72·61	−77 *	17·028	2·33
Purity, mole per cent	96	99·3	—	99·6	99·6
Boiling point, ° C	42·5 at 4 mm Hg	73·5 at 7·5 mm Hg	90·5 at 0·9 mm Hg	86·0 at 4 mm Hg	70·0 at 0·2 mm Hg
Refractive index, n_D^{20}	1·6010	1·5654	1·5320	1·5225	1·5660

* Purity could not be estimated owing to peculiar freezing characteristics.

On heating, polysulphides break down to give a mixture consisting largely of lower polysulphides, including the disulphide, and sulphur. When irradiated with ultra-violet light or heated with an alcoholic solution of sodium sulphide, dimethyl trisulphide undergoes disproportionation and the product contains both disulphide and tetrasulphide. It is probable that a similar reaction takes place on thermal decomposition, but this is largely conjecture, since there is no satisfactory method for distinguishing between higher polysulphides and lower polysulphides containing dissolved sulphur. Mercaptans are usually also formed when polysulphides are thermally decomposed; they are not, however, major products.

As substances capable of reacting with elemental sulphur are equally

well able to react with the loosely combined sulphur of polysulphides, to distinguish between them, especially in the low concentrations in which they are normally present in petroleum distillates, has so far proved impossible. Mercury, alkali cyanides, sulphites, sulphides, and metallic mercaptides give similar reactions with both, the polysulphide at the time being reduced to a lower polysulphide or to the disulphide. The reaction with lead mercaptides provides a convenient method for the removal of polysulphides or sulphur from a too heavily sulphur-treated naphtha. Physical methods, *e.g.*, selective adsorption, have shown some promise in effecting a separation, but the presence of aromatic hydrocarbons makes separation more difficult. Polarography, which has been applied to the determination of elemental sulphur in crude oils, offers a possible solution to the problem, and this we are now investigating. Probably the most reliable method for detecting polysulphides in a low-boiling naphtha is by the effect on the lead response, since elemental sulphur has relatively little effect while, as mentioned above, that of polysulphides is most marked.

Whether the behaviour of Agha Jari crude oil and the others described by Ball, Smith, *et al.*[1] is actually due to elemental sulphur, to polysulphides, or to some other type of sulphur compound of unknown structure yet remains to be determined. So far the types of sulphur compounds identified in petroleum distillates appear to be limited to simple mercaptans, sulphides, thiophenes, and possibly disulphides. No dithiols, cyclic disulphides, or compounds in which there is more than one sulphur atom in the molecule not linked to another sulphur, *e.g.*, dithians, have been recognized. Whether the ketones present in Agha Jari acid sludge [13] have been derived from sulphur bodies of unknown type is doubtful although not impossible, *e.g.*, from thioketones.

The absence of dithiols is hardly surprising in view of the ease with which these compounds oxidize either to cyclic or linear polymeric disulphides. Dithiols would, of course, provide a possible source of the cyclic sulphides, butane-1 : 4-dithiol, for example, being readily converted to thia*cyclo*pentane by the action of heat on its metallic salts :—

In view of the ease with which mercaptans are oxidized with elemental sulphur to disulphides and polysulphides, it is difficult to understand how both could exist together in a crude oil, especially as in some of these nitrogenous bases are present. McMillan and King [42] suggest that the reaction of sulphur with mercaptans is reversible, but offer no satisfactory proof in support. Elemental sulphur is undoubtedly present in some crude oils,[49] and it seems not unreasonable to suppose that polysulphides may also be components of such oils.

Claims have been made that the addition of certain compounds, *e.g.*, cuprous naphthenate,[50] to the crude before distillation will bring about stabilization of the thermally unstable sulphur bodies, so reducing the

sulphur content of the distillate. This claim has not been substantiated with Middle East crudes, but should the unstable bodies prove to be polysulphides, it is difficult to see how they could be stabilized in this manner.

The problem of the composition of the sulphur compounds in petroleum is thus very far from being completely solved, especially in those aspects which concern the polysulphides and the sulphur compounds of higher molecular weight. Much further research will be necessary before answers can be found to the many problems which present themselves. The direct connexion between research of a fundamental nature and the more practical problems of the refiner is not always easy to see, but there can be little doubt of its ultimate value.

Acknowledgments

The author thanks the chairman of the Anglo-Iranian Oil Company for permission to publish some of the results given, and also R. A. Dean, Dr J. N. Haresnape, and other colleagues who have helped in preparing the paper.

References

[1] Hale, J. H., Thompson, C. J., Barker, M. G., Smith, H. M., and Ball, J. S. *Analyt. Chem.*, 1951, **123**, 287.
[2] Birch, S. F., and Norris, W. S. G. P. *J. chem. Soc.*, 1925, **127**, 898.
[3] Thierry, E. H. *J. chem. Soc.*, 1925, **127**, 2756.
[4] Haresnape, D., Fidler, F. A., and Lowry, R. A. *Industr. Engng Chem.* (*Industr.*), 1949, **41**, 2691.
[5] Harbourn, C. L. A., and McAllan, D. T. Unpublished results.
[6] Friedmann, W., and Canseco, C. *Petrol. Refin.*, 1943, **22**, 1.
[7] Friedmann, W., and Rodriguez, C. *Petrol. Refin.*, 1946, **25**, 53.
[8] Polly, O. L., Byrns, A. C., and Bradley, W. E. *Industr. Engng Chem.* (*Industr.*), 1942, **34**, 755.
[9] Nametkin, S. S., and Sosnina, A. S. *Dokl. Ak. Nauk S.S.S.R.*, 1948, **63**, 391.
[10] McAllan, D. T., Cullum, T. V., Dean, R. A., and Fidler, F. A. *J. Amer. chem. Soc.*, 1951, **73**, 3627.
[11] Whitehead, E. V., Dean, R. A., and Fidler, F. A. *J. Amer. chem. Soc.*, 1951, **73**, 3632.
[12] Birch, S. F., Dean, R. A., and Denyer, R. L. Unpublished results.
[13] Birch, S. F., and McAllan, D. T. *J. Inst. Petrol.*, 1951, **37**, 443.
[14] Bougault, J., Cattelain, E., and Chabrier, P. *Bull. Soc. Chim.*, 1940, **7**, 781; cf. Mozingo, R., Wolf, D. E., Harris, S. A., and Folkers, K. *J. Amer. chem. Soc.*, 1943, **65**, 1013.
[15] Bower, J. R., and Cooke, L. M. *Industr. Engng Chem.* (*Anal.*), 1943, **15**, 290.
[16] Brown, R. H., and Meyerson, S. Presented before a Symposium on Non-hydrocarbon Constituents of Petroleum, A.C.S. Meeting, Spring 1952, Milwaukee, Wis.
[17] Cf. "Organic Chemistry," ed. by Gilman, Vol. 1, John Wiley and Sons Inc. (2nd Edition), 96–100.
[18] Kurtz, S. S., and Lipkin, M. R. *Industr. Engng Chem.* (*Industr.*), 1941, **33**, 779.
[19] Landa, S., and Macháček, V. *Coll. Trav. chim. Tchécosl.*, 1933, **5** (1).
[20] Prelog, V., and Seiwerth, R. *Ber.*, 1941, **74**, 1644.
[21] Meerwein, H., Kiel, F., Klösgen, G., and Schoch, E. *J. prakt. Chem.*, 1922, **104**, 161.
[22] Birch, S. F., Dean, R. A., and Whitehead, E. V. Unpublished results.
[23] Treibs, A. *Angew. Chem.*, 1936, **49**, 682; 1940, **53**, 202.
[24] Cf. "Thiophene and its Derivatives," by H. D. Hartough, p. 11. Interscience Publishers Inc., 1952.
[25] Mabery, C. F., and Quayle, W. O. *Amer. chem. J.*, 1906, **35**, 404.
[26] Teutsch, I. *Petrol. Zeit.*, 1934, **30** (20), 1–6.
[27] Friedmann, W. *Ber.*, 1916, **49**, 1344.
[28] Rasmussen, H. E., Hansford, R. C., and Sachanen, A. N. *Industr. Engng Chem.* (*Industr.*), 1946, **38**, 376.
[29] Shepherd, A. F., Henne, A. L., and Midgley, T., Jr. *J. Amer. chem. Soc.*, 1934, **56**, 1355.

[30] Moldavskii, B. L., and Prokonchuk, N. *Zh. prikl. Khim., Leningr.*, 1932, **5**, 619.
[31] Mozingo, R., Harris, S. A., Wolf, D. E., Hoffhine, C. E., Jr., Easton, N. R., and Folkers, K. *J. Amer. chem. Soc.*, 1945, **67**, 2092.
[32] Lochte, H. L., Thomas, E. D., and Truitt, P. *J. Amer. chem. Soc.*, 1944, **66**, 550.
[33] Yur'ev, Yu K., Minachev, Kh. M., and Samurskaya, K. A. *J. gen. Chem., Moscow*, 1939, **9**, 1710.
[34] Crawford, W., and Dean, R. A. Unpublished results.
[35] Yur'ev, Yu K., and Bugorkova, A. A. *J. gen. Chem., Moscow*, 1949, **19**, 720.
[36] Haresnape, J. N. Private communication.
[37] Farlow, M. W., Lazier, W. A., and Signaigo, F. K. *Industr. Engng Chem.* (*Industr.*), 1950, **42**, 2547.
[38] Yur'ev, Yu K., and Tronova, V. A. *J. gen. Chem., Moscow*, 1940, **10**, 31.
[39] Friedmann, W. *J. Inst. Petrol.*, 1951, **37**, 239.
[40] Harbourn, C. L. A. Unpublished results.
[41] Ball, J. S., Rall, H. T., Waddington, G., and Smith, H. M. Presented before a Symposium on the Composition of Petroleum and its Hydrocarbon Derivatives, A.C.S. Spring Meeting, 1951 Cleveland, Ohio.
[42] McMillan, F. H., and King, J. A. *J. Amer. chem. Soc.*, 1948, **70**, 4143.
[43] Holmberg, B. *Ann.*, 1908, **359**, 81.
[44] Birch, S. F., Cullum, T. V., and Dean, R. A. *J. Inst. Petrol*, 1953, **39**, 206.
[45] Schulze, W. A., Short, G. H., and Crouch, W. W. *Industr. Engng Chem.* (*Industr.*), 1950, **42**, 916.
[46] Woodrow, C. G., Carmack, M., and Miller, J. G. *J. chem. Phys.*, 1951, **19**, 951.
[47] Thomas, J. S., and Riding, R. W. *J. chem. Soc.*, 1923, **123**, 3271.
[48] Patel, P. D., Sen-Gupta, I., and Chakravarti, G. C. *J. Indian Inst. Sci.*, 1930, **13A**, 73–84.
[49] Eccleston, B. H., Morrison, M., and Smith, H. M. Presented before a Symposium on Non-hydrocarbon Constituents of Petroleum, A.C.S. Meeting, Spring 1952, Milwaukee, Wis.
[50] Hoover, C. O. U.S.P. 2,472,253, 7 June 1949.

Discussion

Dr E. B. Evans : The paper is of particular interest in that it summarizes a great deal of work over a number of years; work which has been published and also similar work which has not yet appeared in print.

Of particular interest is the positive identification, for the first time, of thiophenes in petroleum distillates. The demonstration of the presence of sulphur compounds consisting of fused five-membered rings is a matter of great importance in relation to the probable constitution of the hydrocarbons present in petroleum.

One of the most useful of the contributions made in the course of the work, however, is the development of the mercuric acetate method introduced by Professor Challenger and his co-workers many years ago and which was further developed by Dr Birch and Mr McAllan recently into a very valuable technique.

Comment on the present paper is a little difficult, as the presentation has been very largely factual, and so many of the statements and the evidence which Dr Birch has produced are quite incontrovertible. He has already replied in advance to many of the points which I had proposed to raise, his presentation having been much fuller than the printed paper.

However, with regard to the separation of thiophenes, it has previously been suggested that, although thiophenes and the mono-substituted thiophenes react readily with mercuric acetate, the di-substituted compounds do not. In the present paper tri-substituted thiophenes seem to have been removed quite readily from kerosine extracts. Has further work demonstrated that di- and tri-substituted thiophenes can, in fact, be made to react with mercuric acetate quite readily ?

Another point of interest is the quantitative aspect. Dr Birch has pointed out that the material with which he and his colleagues have worked has been obtained by sulphuric acid extraction of SO_2 extracts and similar materials. But the kerosine extracts will contain perhaps 1 or 2 per cent of sulphur, corresponding to perhaps three or four times that amount of sulphur compounds. Can Dr Birch give any indication, even approximate, of the relative proportions of dialkyl sulphides, cyclic sulphides, thiophenes, and soon, which will occur in a Middle East kerosine extract? That would be a point of very considerable interest to most petroleum chemists.

Dr Birch has referred to nomenclature. He explained, but I noted that he did not attempt to justify, the thia system, now widely accepted in the States. I have, perhaps, rather stronger views on this subject. I object most particularly to the terms " thia*cyclo*pentane " and " thia*cyclo*hexane." That kind of nomenclature is justified or, shall we say, legalized by the International Union rules, but to petroleum chemists in general the word " pentane," whether prefixed by " *cyclo* " or anything else, indicates a five-carbon hydrocarbon. It may be legal to replace a CH_2 by a sulphur and call the result a " thia " hydrocarbon, but it is a very confusing nomenclature. It is still true, as Dr Clarence Smith remarked to the Chemical Society in 1936, that the nomenclature of organic compounds containing sulphur is in a chaotic state. I still prefer the " polymethylene " nomenclature, which is easier to understand and will convey more to the petroleum chemist than the " thia " nomenclature. " Tetramethylene sulphide " conveys much more to me than " thia*cyclo*pentane," and the same applies to the six-membered ring compounds. The term " thiophane " is not entirely satisfactory, except as a generic term, because of the difficulty of applying it to six-membered rings. I do not see any objection to retaining the old " polymethylene " nomenclature.

Perhaps Dr Birch will give his own views on this question. The " thia " nomenclature is probably unfamiliar to most petroleum chemists.

One very interesting point in the paper is that concerning the detection of the thia-analogue of adamantane. So far as I am aware, adamantane itself has been detected only in one naphtha. It is an extraordinary compound, and it is probably unique as, I believe, the only organic compound which crystallizes in the cubic system. Dr Birch did refer to the crystallographic examination of the thia-analogue; does that crystallize similarly? The refractive index of adamantane itself is quite high for a hydrocarbon, about 1·58, and the melting point about 268° C. Any further information on the properties of the thia compounds would be interesting.

We should all appreciate the amount of work which has gone into the accumulation of the data presented by Dr Birch. Some thirty to forty sulphur compounds have been fairly definitely established as present in petroleum naphthas. It is not only a matter of separation of these materials but a lot of synthetic work is also needed to obtain compounds of known constitution, in order to make comparisons with physical data.

DR BIRCH : It would be best for Mr Dean to answer Dr Evans' question regarding the reactions of thiophenes and mercuric acetate, since he and Mr Denyer have been concerned with the investigation of kerosine extract acid sludge.

R. A. DEAN : Any thiophene with a vacant α position will react readily with mercuric acetate solution to form a mono- or poly- acetoxy-mercuric derivative, depending upon the substitution of the other positions in the thiophene nucleus. Thiophene, for example, will form a tetra-acetoxy-mercuric compound. The tri-substituted thiophenes isolated from kerosine extract tar oil all had vacant α positions and readily formed a mono-acetoxy-mercuric compound. 2 : 5-Dimethylthiophene, with only β positions vacant, reacts very slowly to form a diacetoxy-mercuric derivative, but 2 : 3 : 5-trimethylthiophene, with only one vacant β position, reacts quite readily to form a monoacetoxymercuric compound. Tetramethylthiophene, being incapable of reaction, was readily separable by this means from the other compounds with which it was associated.

DR BIRCH : I agree with Dr Evans in his comments on the thia-nomenclature. It is particularly difficult to form a mental picture of such compounds as dimethyl tetrasulphide when referred to as 2 : 3 : 4 : 5-tetrathiahexane. With this system sulphur itself, consisting of a ring of eight sulphur atoms, could very well be described as octathia*cyclo*-octane ! The advantage of the thia system is appreciated when referring to substituted thia*cyclo*-pentanes and -hexanes which, with the old polymethylene system, become very involved. It is certainly much easier to talk of " thia-adamantane " than to use the Geneva nomenclature.

With regard to the hydrocarbon adamantane itself, although several grams were prepared, its physical properties were not determined and the infra-red absorption did not show any particular characteristic band, which is in line with its symmetrical structure. Its preparation followed closely the synthesis outlined by Prelog. Instead of starting with dimethyl malonate in the first step as described by Meerwein, the more readily available diethyl ester was used, and very low yields of impure material were obtained. Only when the dimethyl ester was tried could the earlier work be repeated. I mention this to avoid others wasting time and effort in making the same mistake.

The crystalline structure of thia-adamantane is now being investigated by Professor Lonsdale at University College. It has been found to be isomorphous with adamantane.

DR EVANS : Have you any quantitative data concerning the various sulphur bodies present in the kerosine extract ?

DR BIRCH : I am afraid not. The acid treatment was carried out in Abadan, and the sulphur bodies recovered from the sludge by dilution with water sent here for examination. The final concentration and purification of the sulphur bodies did not lend itself to any reliable quantitative estimation of individual compounds.

DR M. BENGER : It was found in Abadan that the crude mixture of sulphur compounds recovered from the dilution of benzene extract sludge possesses useful inhibitive properties when added to the acid used to treat wells. Have you any explanation for this being found ?

DR BIRCH : No. We have presumed the effect to be due partly to the formation of sulphonium derivatives and partly to the presence of soluble sulphonic acids.

E. H. SADLER : I was wondering whether, in a naphthenic crude, cyclic sulphides predominate, while in paraffinic crudes, open chain compounds do.

DR R. W. SAVILLE : In the preparation of polysulphides from disulphides, what concentration of base was employed ? This is of interest, since excess of the base is known to reverse the reaction and reform the disulphide.

It would be interesting to know whether, since dithiols are absent, any cyclic disulphides have been isolated ?

Finally, in view of the known ready-base-catalysed oxidation of mercaptans by sulphur, their co-existence with cross-linked sulphides in presence of bases may be due to depletion of the sulphur itself by direct sulphur-base interaction.

DR BIRCH : In our preparations we have only used secondary bases in catalytic quantities say of the order of 2 to 5 per cent.

Cyclic disulphides have not so far been detected in any petroleum distillates. Both they and dithiols are very characteristic in their behaviour, and there should be little difficulty in detecting them. It is very unlikely that either would survive extraction with acid and could hardly be expected in the sulphur bodies recovered from acid sludge.

So far no sulphur bodies likely to form cross-linkage have been found in petroleum.

W. T. LYN : Are all the different types of sulphur compounds equally harmful from the consumer's point of view ?

DR BIRCH : After elementary sulphur, mercaptans are probably the most harmful. Alkyl sulphides on the whole are much less likely to give trouble than disulphides. In an account of our work on polysulphides * we have shown that disulphides, on irradiation with ultra-violet light or sunlight, or during thermal treatment, break down to give RS radicals. How far radicals of this type are responsible for some of the objectionable characteristics of sulphurous distillates is as yet unknown. They are capable of initiating chain reactions, and are almost certainly associated with gum formation. Mercaptans are also able to form RS radicals, and for the same reason cause trouble. We have not been able to produce radicals from polysulphides, probably because when these compounds break down elemental sulphur is formed, which acts as a chain stopper. Sulphur formed in this way would be corrosive. Polysulphides themselves have an adverse effect on lead response.

THE PRESIDENT : I am sure everyone present will wish to join with me in thanking Dr Birch very much indeed for his most interesting paper. I cannot claim that I understood all of it, but certainly found parts of it most interesting, more particularly when he dealt with the matter of the sulphur in crude oil; from the production angle that is one of the most important problems.

(The vote of thanks was heartily accorded.)

---

* *J. Inst. Petrol.*, 1953, **39**, 206.

THE PREPARATION AND PROPERTIES OF DI-ALKYL DI- AND POLY-SULPHIDES. SOME DISPROPORTIONATION REACTIONS

By S. F. Birch, T. V. Cullum, and R. A. Dean *

Summary

The investigation into the preparation and properties of sulphur compounds similar in type to those present in the lower boiling petroleum distillates has been extended to dialkyl di- and higher poly-sulphides.

The preparation is described and the physical properties are given for the following compounds: disulphides—methylethyl, methyl-*tert*-butyl, di-*n*-butyl, and 1 : 2-dithian; trisulphides—dimethyl, diethyl, di-*n*-butyl, and di-*tert*-butyl; tetrasulphides—di-ethyl, di-*n*-butyl, and di-*tert*-butyl.

The difficulty of preparing methyl ethyl disulphide in a pure state has been noted in a previous communication.[3] This has now been shown to be due to a photochemical disproportionation reaction, and a pure sample of methyl ethyl disulphide has been obtained by excluding light during distillation. Data are presented on the disproportionation reactions of other disulphides and the effect of light on some polysulphides.

In the course of an investigation in progress in these laboratories dealing with the chemical and physical properties of sulphur compounds likely to be present in petroleum distillates or to be formed during refining operations, a number of di-alkyl disulphides and the corresponding polysulphides have been prepared and studied. The results are described in the present paper.

While no evidence has so far been produced for the presence of dialkyl di- or higher poly-sulphides in petroleum distillates which could not have resulted from secondary reactions, *e.g.*, oxidation of mercaptans by oxygen or elemental sulphur, there is ample evidence that compounds of this type are formed during sweetening and certain desulphurization reactions. The formation and chemical behaviour of such sulphur bodies is consequently of considerable interest. Disulphides and particularly polysulphides, for example, have a marked effect upon lead response, and their presence in motor and aviation fuels is consequently to be avoided.[1, 2]

The preparation and properties of a number of symmetrical dialkyl disulphides have been described in an earlier paper of this series [3] which also included an account of some of the corresponding unsymmetrical compounds. The former were obtained by the oxidation of the appropriate mercaptans and the unsymmetrical derivatives by two additional routes, one of which involved the reaction of a mercaptan with a disulphide in alcoholic solution in the presence of a trace of alkali. This last reaction has now been considerably extended and conditions for optimum yields have been established, while at the same time a number of interesting observations on the general behaviour and properties of these compounds have been made. It has also been shown that unsymmetrical disulphides can be obtained by a photochemical reaction. This has been described in the second part of the paper. Whilst this work was in progress, a U.S. patent [4] appeared in which

* Research Station, Anglo-Iranian Oil Company Ltd., Sunbury-on-Thames, Middlesex.

the preparation of many disulphides by the irradiation of mixtures of disulphides and mixtures of disulphides with mercaptans was described.

Preparative Methods

(a) *Symmetrical Disulphides*

These compounds were prepared as previously described.[3]

(b) *Unsymmetrical Disulphides*

Three methods were employed in the preparation of these compounds :—

(I) Oxidation of equimolar mixtures of the appropriate mercaptans—

$$RSH + R'SH + \tfrac{1}{2}O_2 = R'SSR + H_2O$$

(II) Reaction of a mercaptan with a disulphide in alkaline alcoholic solution—

$$RSH + R'SSR' \rightleftharpoons R'SSR + R'SH$$

(III) Reaction of two disulphides in alkaline solution using a trace of mercaptan as catalyst—

$$RSSR + R'SSR' \rightleftharpoons 2R'SSR$$

Method (I) using hydrogen peroxide, iodine, or potassium ferricyanide as oxidizing agent gave a theoretical yield of a mixture of the three possible disulphides, from which the required unsymmetrical compound was separated by distillation. When, however, a tertiary mercaptan was involved, it was found necessary to employ potassium ferricyanide, since, with this type of mercaptan, oxidation with hydrogen peroxide tends to proceed beyond the disulphide stage,[3] while with iodine there is a tendency for sulphenyl iodides to be formed [5, 6] which decompose and contaminate the product. The second method (II) was applicable in most cases, but failed in the reaction of di-*tert*-butyl disulphide with both *tert*-amyl mercaptan and thiophenol owing to the slowness of the reaction. Method (III) was only used when the required disulphides happened to be available, and was consequently not as fully investigated as the others. Methods (II) and (III) have been described in recent patents [7–10] which also disclose the use of sodium sulphide and anhydrous hydrogen halides as catalysts.

The molar ratios of the three disulphides formed by the oxidation of an equimolar mixture of mercaptans of varying types is shown in Table I. The ratios are only approximate because the method of analysis, involving fractionation of the reaction products, was not precise.

The ratios of symmetrical to unsymmetrical disulphides obtained probably represent a close approach to the equilibrium values. If all recombinations of RS and R'S have an equal probability, a ratio of 1 mol of each symmetrical to 2 mols of the unsymmetrical disulphide would be obtained, and this ratio is found when the mercaptans from which the disulphides are formed are of similar type, *i.e.*, both primary or both tertiary. Significant departures from this ratio are observed when RS and R'S are different, *e.g.*, primary and tertiary, the ratio being greatly in favour of the unsymmetrical compound, which suggests that the free energy of the product is then less than the mean of the free energies of the

two symmetrical compounds. The ease of oxidation of mercaptans based upon data recently published [11, 12] is in the order: aromatic > primary > secondary > tertiary, the tertiary being the most difficult to oxidize. A comparison of this series with the ratios given above suggests that the greater the difference between the oxidation–reduction potentials of the two

TABLE I

Method of preparation	Reactants	Molar ratio of each *sym* to *unsym* disulphide in product
(I)	Methyl mercaptan Ethyl mercaptan	1 : 2
(III)	Dimethyl disulphide Diethyl disulphide	1 : 2
(I)	Ethyl mercaptan *n*-Propyl mercaptan	1 : 2
(I)	Ethyl mercaptan *n*-Butyl mercaptan	1 : 2
(III)	Diethyl disulphide Di-*n*-butyl disulphide	1 : 2
(III)	Diethyl disulphide Di-*iso*butyl disulphide	1 : 2
(II)	Diethyl disulphide *n*-Butyl mercaptan	1 : 2
(I)	Ethyl mercaptan *sec*-Butyl mercaptan	1 : 4·5
(II)	Dimethyl disulphide *tert*-Butyl mercaptan	1 : 5
(II)	Diethyl disulphide *tert*-Butyl mercaptan	1 : 6
(II)	*n*-Octyl mercaptan Di-*tert*-butyl disulphide	1 : 4
(I)	*tert*-Butyl mercaptan *tert*-Amyl mercaptan	1 : 2
(I)	*tert*-Butyl mercaptan Thiophenol	1 : 8
(II)	Thiophenol Dimethyl disulphide	1 : 3

mercaptan disulphide systems the larger is the amount of the unsymmetrical disulphide formed compared with the symmetrical compounds, and that when the relative potentials are the same the ratio is 1 : 2.

The slow rate experienced in the reaction of *tert*-amyl mercaptan and thiophenol with di-*tert*-butyl disulphide can be explained on steric grounds. If the reaction in methods (II) and (III) is visualized as proceeding by the attack of a mercaptide ion upon a disulphide molecule,

$$RS^- + R'SS'R' \longrightarrow R'S^- + RSSR'$$

it is reasonable to assume that the sterically hindered mercaptide ions would have difficulty in approaching the S–S bonds of a di-*tert*-alkyl disulphide or a diphenyl disulphide molecule. This would not apply with *n*-octyl mercaptan and di-*tert*-butyl disulphide or thiophenol and dimethyl disulphide. Furthermore, if the reaction involved in method (I) proceeds by a mechanism of the type suggested by Michaelis and Schubert [13]

i.e.,

$$RS^- + X \longrightarrow RS + X^-$$
$$2RS \longrightarrow R_2S_2$$

where X represents the oxidizing agent, approach of a mercaptan ion to a disulphide molecule is not required, and the reaction should not be affected by these particular steric considerations. It can then be assumed that this method will give the equilibrium value for the reaction.

(c) *Dialkyl Polysulphides*

The stability of these compounds, which have not been as fully studied as the disulphides, decreases rapidly with increasing sulphur chain, with the result that although a number of trisulphides and tetrasulphides have been isolated, no satisfactory method has been reported for the purification and preparation of the higher members. The lack of stability is shown by the ease with which they lose sulphur to such reagents as mercury, caustic soda, and sodium sulphide and decompose to form lower polysulphides and elemental sulphur.* These reactions and the structure of polysulphides have been discussed recently by Foss.[14]

Three general methods were investigated for preparing polysulphides :—

(1) Action of sulphur chlorides,[15] thionyl chloride,[16] or sulphuryl chloride [17] on mercaptans

$$2RSH + S_2Cl_2 \longrightarrow RS_4R$$

(2) By the reaction of elemental sulphur or alkali metal polysulphides with dialkyl di- or tri-sulphides [18, 19]

$$R_2S_2 + nS \longrightarrow R_2S_{n+2}$$

(3) From alkyl halides [20] or sulphates [21] by reaction with sodium or potassium polysulphides

$$2RX + Na_2S_n \longrightarrow R_2S_n + 2NaX$$

The first method, as described by Holmberg,[16] was used for the preparation of the polysulphides in the present work, with the exception of dimethyl trisulphide, which was prepared by an alternative route involving the oxidation of the Bünte salt in the presence of sodium thiosulphate.[3] Thionyl chloride rather than sulphur dichloride was used for the preparation of trisulphides, since when the last is employed small amounts of higher polysulphides containing more than three sulphur atoms are also formed. Purified monochloride [22] gives only the tetrasulphide under the conditions given below, although it is claimed by Patel *et al* [23] that a hexasulphide can be obtained using this reagent. The application of the second method to the preparation of di-*tert*-butyl trisulphide has recently been described,[24] although a less pure product was obtained than by the thionyl chloride method used by ourselves. This sulphurization reaction has also been subject of patent literature,[25–27] which has described the use of amines and phosphorus sulphides as catalysts for the reaction as well as ammonia as reported by Holmberg.[16] Our observations indicated that secondary

* Under suitable conditions, for example when mercaptides are oxidized with sulphur in the presence of relatively large volumes of petroleum naphthas, higher polysulphides, possibly containing six and even more sulphur atoms in a chain, are probably formed and pass into the hydrocarbon phase, where, in high dilution, they appear to remain undecomposed. Evidence for this is the unexpectedly low lead response shown by some plumbite-treated naphthas, which appears to be more marked than the actual sulphur content would warrant.

TABLE II

Compound	Boiling point		n_D^{20}	d_D^{20}	Freezing point, °C	Freezing point, for zero impurity, °C	Purity, mol per cent	Remarks
	°C,	mm Hg press.						
Disulphides								
Methyl ethyl disulphide	58	57	1·5146	1·0224	−90·25	−89·83	99	
Methyl *tert*-butyl disulphide	69	42	1·4975	0·9626	−51·333	−51·197	99·62	
Di-*n*-butyl disulphide	85	3	1·4923	0·9371	—*	—	—	d^{25} 0·9231
Di-*tert*-butyl disulphide	88	21	1·4899	0·9226	− 5·055	− 4·95	99·77	Hf 3·14 k.cal/mol
tert-Amyl *tert*-butyl disulphide	97	13	1·4943	0·9291	−58·197 1st phase −58·231 2nd phase	—	—*	Two phases shown on f.p. curve
Di-*tert*-amyl disulphide	98	5	1·4988	0·9342	—†	—	—	h_D^{25} 1·4965, d^{25} 0·9304
Polysulphides								
Dimethyl trisulphide	42·5	4	1·6010	1·2013	−69·68	−68·05	96	d^{25} 1·1978
Diethyl trisulphide	57	3	1·5654	1·1082	−72·83	−72·61	99·3	
Di-*n*-butyl trisulphide	90·5	0·9	1·5320	1·0180	−77	—	—*	
Di-*tert*-butyl trisulphide	86	4	1·5225	0·9922	+16·63	+17·028	>99·6	d^{25} 0·9881
Diethyl tetrasulphide ‡	About 62 (decomp)	0·25	1·1655	—	—	—	—	
Di-*n*-butyl tetrasulphide ‡	Decomp	—	1·5722	—	—	—	—	
Di-*tert*-butyl tetrasulphide	70	0·2	1·5660	1·0690	+ 1·846	+ 2·33	>99·5	d^{25} 1·0640

The cryoscopic constants used for calculation of purity were estimated from the time of freezing with the exception of that for di-*tert*-butyl disulphide which was calculated from the latent heat of fusion.

* The shape of the cooling curve was such that no purity estimation could be made.

† This compound set to a glass on cooling.

‡ These compounds were probably impure.

amines were more efficient catalysts for the reaction than pyridine or aromatic amines but that all these amines catalysed the reaction of sulphur with disulphides at 120° C, which did not occur in their absence. The third method gives a mixture of various polysulphides, since the alkali metal polysulphides are of indefinite composition. Thomas *et al* [28] claim that potassium pentasulphide can be prepared as an individual compound and that this reacts with an alkyl halide to give a pure dialkyl pentasulphide.[20] In our experience this method yielded a product containing a high polysulphide contaminated with lower polysulphides.

An attempt to purify dialkyl tri- and tetra-sulphides through the urea-adducts which are readily formed by the straight-chain derivatives was not successful, the polysulphides recovered from the adduct invariably containing a small amount of non-adductable material, presumably consisting of lower polysulphides, formed by decomposition.

The physical properties of the disulphides and polysulphides prepared during the course of the present work are given in Table II.

Free Radical Formation by Sulphur Compounds

In attempting to prepare pure methyl ethyl disulphide from the impure material obtained by the oxidation of equimolar mixtures of methyl and ethyl mercaptans, it was found that, on fractionation through a forty-plate glass-packed column, complete disproportionation occurred and the only products obtained were dimethyl and diethyl disulphides. The reason for this was not at first obvious, and several possible causes, such as the presence of traces of compounds thought to be capable of catalysing the decomposition, *e.g.*, halides, were investigated without success. Eventually it was found that if light was excluded during the fractionation, no disproportionation occurred and pure methyl ethyl disulphide could be obtained, which suggested a free radical reaction resulting from the formation of RS radicals by photochemical fission of the disulphide molecule. This hypothesis was confirmed by the irradiation of methyl ethyl disulphide in a petroleum ether solution containing acrylonitrile,* which remained clear in the dark but started to form a precipitate immediately upon exposure to sunlight and rapidly formed a dense mass of polymer. This test confirmed the formation of free radicals by this disulphide upon exposure to light.

A series of sulphur compounds was examined by this method, and in Table III an approximate visual comparison of the amount of macropolymer formed with the different compounds is indicated. All experiments were carried out in pyrex vessels except where a Q appears, which indicates that a quartz vessel was used.

Polymerization was shown to occur when disulphides were heated with acrylonitrile in the dark under pressure at 150° C. No polymerization occurred at 100° C. This is in agreement with the disproportionation reaction between *n*-decyl mercaptan and di-*n*-propyl disulphide reported by Gorin *et al.*[30]

The disulphides show the greatest tendency to polymerize acrylonitrile. Within this class of compounds the only significant difference between

* The polymerization of acrylonitrile under such conditions is an indication of the formation of free radicals.[29]

individual compounds is the much greater tendency of diphenyl disulphide to cause polymerization than of any other disulphide. The tendency of diphenyl disulphide to form free radicals has, of course, been discussed previously [31] because of its thermochromatic behaviour, and this has been confirmed by Schönberg.[32–34] The formation of free radicals from 2 : 2′-benzthiazyldisulphide has been demonstrated by Cutforth and Selwood by means of magnetic measurements.[35]

TABLE III

Sulphur compound	Extent of polymerization when irradiated by		
	Ultra-violet light	Bright sunlight	Diffuse daylight
Mercaptans			
Ethyl	Q X	X	D
n-Propyl	Q X	—	—
*iso*Propyl	Q X	X	D
n-Butyl	Q X	X	D
tert-Butyl	Q DDD	D	D
n-Octyl	Q X	D	D
Phenyl (Thiophenol)	Q X	D	D
Disulphides			
Diphenyl	Q DDD	DDD	D
Dimethyl	Q DDD	DD	D
Methyl ethyl	Q DDD	DD	D
Diethyl	Q DDD	DD	D
Di-*iso*propyl	—	DD	—
Ethyl *n*-butyl	—	DD	—
Ethyl *tert*-butyl	Q DDD	DD	D
Methyl *tert*-butyl	—	DD	—
Di-*sec*-butyl	—	DD	—
Di-*n*-butyl	—	DD	—
Di-*tert*-butyl	Q DDD	DD	D
Trisulphides			
Dimethyl	—	X	—
Diethyl	—	X	—
Di-*n*-butyl	—	X	—
Di-*tert*-butyl	—	DDD	—
Tetrasulphides			
Diethyl	X	X	—
Di-*n*-butyl	Q X	X	—
Di-*tert*-butyl	Q X	X	—

X indicates no polymerization, D slight polymerization, DD fairly heavy polymerization, DDD very heavy polymerization of the acrylonitrile.

The only polysulphide capable of forming the macro-polymer of acrylonitrile was di-*tert*-butyl trisulphide. Other polysulphides undoubtedly initiate the polymerization under these conditions, but the absence of the macro-polymer can be explained by the fact that they readily form sulphur, which is an efficient inhibitor of acrylonitrile polymerization. This inhibiting effect was confirmed when diphenyl disulphide, contaminated with a small amount of a mixture of diethyl tri- and tetra-sulphides, did not cause polymerization of acrylonitrile on exposure to light. Since the addition of elemental rhombic sulphur decreased the rate of polymerization

but did not completely inhibit it, it appears that the sulphur formed by polysulphide decomposition is far more effective. Di-*tert*-butyl trisulphide is the only polysulphide that does not react with plumbite/mercaptan solution or ammonium sulphide solution [36] as if it contained elemental sulphur.

Mercaptans are also rather anomalous in their behaviour to acrylonitrile. This again is probably due to elemental sulphur formed on their decomposition.[37] In diffuse daylight they all promote polymerization, but with ultra-violet irradiation only *tert*-butyl mercaptan causes polymerization. Under these conditions of irradiation, *tert*-butyl mercaptan does not decompose to give sulphur, whereas *n*-propyl mercaptan has been shown to do so.

Photochemical Disproportionation Reactions

The observation that disproportionation of methyl ethyl disulphide occurs during fractionation led to an investigation of the photochemical disproportionation reactions of disulphides and polysulphides.

The disproportionation of methyl ethyl disulphide during distillation where no attempts have been made to exclude light has been described above. Under fractionation conditions one compound, dimethyl disulphide, is continuously removed and the equilibrium of the reaction

$$R_2S_2 + R_2'S_2 \rightleftharpoons 2R'SSR$$

is forced to one side to give complete disproportionation to the symmetrical disulphides. The reversibility of the reaction is clearly demonstrated by the fact that irradiation of an equimolar mixture of dimethyl and diethyl disulphides with ultra-violet light at room temperature gave a product which was a mixture of dimethyl, methyl ethyl, and diethyl disulphides.

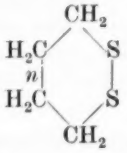
In view of the ease with which the disproportionation reaction took place, the stability of a pure sample of methyl ethyl disulphide (99·2 mol per cent, f.p. −90·15° C) under storage conditions was investigated. When exposed to bright sunlight in a clear soda-glass bottle at room temperature the purity decreased, and after 20 hr was considerably less than 90 per cent. When stored in the dark at room temperature the stability was reasonable, but a slow decrease in purity occurred; after six months the purity fell to 99·0 mol per cent and after eleven months to 98·7 mol per cent. This decrease in purity cannot be accounted for by inaccuracies in the determination, and it seems probable that in the dark a slow thermal disproportionation reaction takes place.

Methyl *n*-butyl and methyl *n*-propyl disulphides were both prepared by irradiation of a mixture of the two appropriate symmetrical disulphides with ultra-violet light, and upon irradiation by ultra-violet light a pure sample of the methyl *n*-butyl disulphide was shown to disproportionate into a mixture of the three disulphides. A sample of ethyl *n*-propyl disulphide which had been stored for two years at room temperature without any special precautions being taken to exclude light had also disproportionated into a mixture of the three disulphides.

Attempts to prepare methyl *tert*-butyl, ethyl *tert*-butyl, and *tert*-butyl *tert*-amyl disulphides by irradiation of mixtures of the corresponding symmetrical disulphides were completely unsuccessful, none of the unsym-

metrical compounds being formed. Neither did the three unsymmetrical disulphides on irradiation by ultra-violet light yield any of the two appropriate symmetrical disulphides.

Irradiation of the monomeric cyclic disulphide obtained by the oxidation of butane-1 : 4-dithiol converted it into an insoluble polymeric compound. It is probable that opening of the ring occurs with formation of a diradical which recombines to form a linear polymer :—



$$\longrightarrow \quad (\cdot SCH_2 \cdot CH_2CH\ CH_2S\cdot)_n$$

Irradiation of dimethyl trisulphide by ultra-violet light yielded in addition to recovered trisulphide a small amount of the disulphide and the tetrasulphide. Similar results were obtained with di-*tert*-butyl tri- and tetrasulphides, although the reaction was only very slight with the former.

The mechanism of these photochemical disproportionation reactions can be attributed to a free radical process. The peroxide catalysed photochemical reaction of mercaptans with olefines has been shown to be a free radical reaction,[38] and it seems reasonable to assume that light of wavelength 3000 to 4000 Å would be capable of promoting fission of the S–S bonds of disulphides, since the S–S bond strength is of the order of 70 to 75 k.cal/mol.[39]

In view of the very extensive reaction that occurs upon irradiation, and particularly the complete disproportionation of the methyl ethyl disulphide upon fractionation in diffuse daylight, the quantum efficiency of the reaction

$$2RSSR' \longrightarrow RSSR + R'SSR'$$

must be considerably higher than unity. It is suggested that for the di-primary alkyl disulphides, a chain reaction of the type

$$RSSR \xrightarrow{h\nu} 2RS$$

$$RS + RSSR' \longrightarrow R'S + RSSR$$

$$R'S + + RSSR' \longrightarrow RS + R'SSR', \text{ etc.}$$

occurs, chain initiation being by cleavage of the S–S bond, and chain termination by recombination of radicals to form a disulphide. The absence of a disproportionation reaction between a di-primary and a di-tertiary alkyl disulphide or by a primary tertiary alkyl disulphide points to a drastic shortening of the reaction chain in these cases, since the acrylonitrile reaction shows that the primary formation of RS radicals occurs with these compounds. It was at first thought that the chain reaction was non-operative for the reason that one of the radicals formed has insufficient energy to break the S–S bond of the other disulphide molecule. The absence of any disproportionation reaction between di-*tert*-butyl and di-*tert*-amyl disulphides, the radicals from which would presumably have very similar energies, showed that this was not so and that the absence of disproportionation reactions must be due to the inability of

the bulky *tert*-alkyl radical to approach and react with another disulphide molecule. This steric factor probably accounts for the greater difficulty of reduction of di-*tert*-butyl disulphide.[40]

The disproportionation reactions shown by polysulphides are presumably of a similar nature, *e.g.*,

$$\mathrm{R{-}S{-}S{-}S{-}R} \longrightarrow \begin{matrix}\mathrm{R{-}S{-}S} \\ \downarrow \\ \mathrm{RSSSSR}\end{matrix} + \begin{matrix}\mathrm{RS} \\ \downarrow \\ \mathrm{RSSR}\end{matrix}$$

$$\mathrm{R'S} + \mathrm{R{-}S{-}S{-}S{-}R} \longrightarrow \mathrm{RSSR} + \mathrm{R'SS}, \text{ etc.}$$

The reaction is undoubtedly complicated by degradation of the radicals to give atomic sulphur

$$\textit{e.g.}, \mathrm{RSS^{\circ}} \longrightarrow \mathrm{RS^{\circ}} + \mathrm{S}$$

which inhibits the formation of a polymer from acrylonitrile. This facile formation of sulphur and radicals explains the almost quantitative conversion of diethyl tetrasulphide to diethyl trisulphide upon fractionation at a low temperature (100° C) and our inability to prepare a pure sample of di-*n*-butyl tetrasulphide. It is apparent that the *tert*-alkyl grouping confers considerable strength to the S–S bonds, since the trisulphide does not readily lose its sulphur, whilst the tetrasulphide can be distilled under reduced pressure at 80° to 100° C without decomposition.

Experimental

(a) *Preparation of Disulphides*

Symmetrical disulphides were obtained by the method described previously.[3] Unsymmetrical disulphides were prepared by one of the three methods outlined above. Purification was effected by fractionation in the absence of light using a forty-plate glass packed column operating under reduced pressure.

(b) *Preparation of Polysulphides*

(1) *Dimethyl Trisulphide.*—This was prepared as previously described [3] by the oxidation of the Bünte salt with iodine in a solution containing sodium thiosulphate. The effect of the presence of varying amounts of the thiosulphate on this reaction is shown in Table IV, which gives the yield of polysulphides obtained. Products were worked up as usual and analysed by distillation.

Table IV

Molecular excess of thiosulphate over halide used, per cent	Mol per cent product based upon mols halide used		
	Disulphide, per cent	Trisulphide, per cent	Tetrasulphide, per cent
1	76	Trace	—
7·5	61	21	—
33	35	32	3
66·6	16	43	14

(2) *Diethyl Trisulphide.*—Thionyl chloride (1 mol) was added dropwise, with vigorous stirring, to a solution of the thiol (4 mol) in ether (2000 ml). The mixture was stirred for 1 hr after addition was complete and worked up in the usual manner. The di- and tri-sulphide (95 per cent yield) were separated by fractional distillation in a twenty-plate glass packed column under reduced pressure (3 to 5 mm Hg).

(3) *Di-tert-butyl Trisulphide.*—This was prepared in a similar way to the diethyl trisulphide using dry benzene instead of ether. The di- and tri-sulphides (88 per cent yield) were separated by fractional distillation through a ten-plate glass-packed column under reduced pressure (4 mm Hg).

(4) *Di-n-butyl Trisulphide.*—This was prepared in the same manner as the diethyl compound in 95 per cent yield. On fractionation slight decomposition occurred, and it was necessary to redistil 1 mm Hg pressure to obtain a satisfactory material.

(5) *Diethyl Tetrasulphide.*—Sulphur monochloride (0·27 mol) dissolved in dry carbon disulphide was added slowly to a cooled stirred solution of thiol (0·55 mol) in carbon disulphide. The solvent was removed by distillation under reduced pressure at room temperature. The yield of crude tetrasulphide was in the region of 85 to 90 per cent based on the thiol used. Attempts to obtain a pure sample of the tetrasulphide by distillation under reduced pressure from a Claisen flask were unsuccessful, the distillate appearing to consist of a mixture of trisulphide, tetrasulphide, and higher polysulphides.

(6) *Di-tert-butyl Tetrasulphide.*—Sulphur monochloride (0·27 mol) dissolved in dry benzene was added to a stirred and cooled solution of the thiol (0·55 mol) in benzene. Stirring was continued for 1 hr after addition was completed and the solvent then removed at room temperature under reduced pressure. Distillation of the residue (1 mm Hg pressure) gave the pure compound in 90 per cent yield.

(7) *Di-n-butyl Tetrasulphide.*—A crude material was prepared as described for the di-*tert*-butyl compound in 98 per cent yield. All attempts to purify it by distillation were unsuccessful, including distillation in a molecular still at 30° C. Attempts at purification through the solid urea adduct also failed, since re-adduction of the regenerated tetrasulphide always gave a small amount of non-adducted lower refractive index material presumably due to a slow equilibration of the tetrasulphide at room temperature into a mixture of di- and higher polysulphides.

(c) *Disproportionation of Dimethyl Trisulphide*

(1) *In Alcoholic Solution.*—Dimethyl trisulphide (12·6 g, 0·1 mol) was dissolved in ethanol (35 ml) and an aqueous solution (2 ml) of sodium sulphide (0·0008 mol) added. The mixture was refluxed for 14 hr, diluted with water, and extracted with petroleum ether (<40° C). Distillation at 1 mm Hg pressure gave impure dimethyl disulphide (2 g), impure trisulphide (5·3 g), and impure tetrasulphide (3 g). Similar results were obtained using a trace of mercaptan and alkali in place of the sodium sulphide; no reaction took place when the sodium sulphide solution was replaced with concentrated hydrochloric acid (0·2 ml).

(2) *By U.V. Irradiation.*—Dimethyl trisulphide (10 g) was placed in a small water-cooled quartz tube and irradiated for 8 hr with an U.V. lamp

(Hanovia U.V. S500) at a distance of 10 cm. The product was distilled at 2 mm Hg pressure, yielding impure disulphide (1 g), trisulphide (7 g), and tetrasulphide (1·5 g).

(d) *Preparation of Unsymmetrical Disulphides by Irradiation*

(1) *Methyl ethyl disulphide.*—A mixture of dimethyl disulphide (188 g) and diethyl disulphide (244 g) was placed in a transparent silica tube, maintained at 20° C by an external silica water jacket, and irradiated for 5 hr with light from an U.V. lamp (Hanovia U.V. S500) placed at a distance of 8 cm. The product was fractionated without further treatment in a twenty-plate glass-packed column at 55 mm pressure in the absence of light.

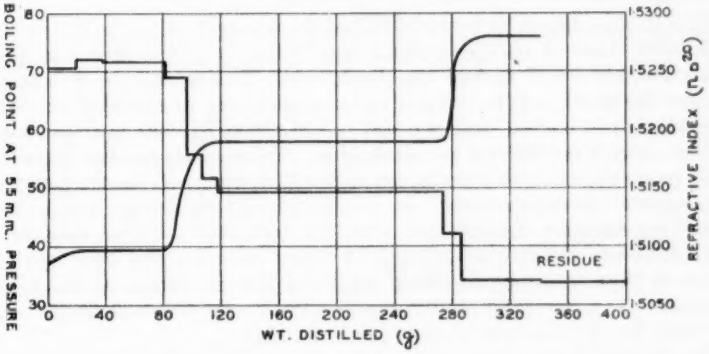


FIG 1

FRACTIONATION OF THE PRODUCT FROM THE IRRADIATION OF A MIXTURE OF DIMETHYL AND DIETHYL DISULPHIDES

The distillation curve (Fig 1) shows three plateaux corresponding with the two symmetrical and the unsymmetrical compounds.

(2) *Methyl*-n-*propyl Disulphide.*—A mixture of dimethyl disulphide (188 g, 2·0 mol) and di-*n*-propyl disulphide (300 g, 2·0 mol) was irradiated in a water-cooled quartz tube by means of a 500-watt U.V. lamp for 6 hr. The product was fractionated in a twenty-plate glass-packed column at a pressure of 20 mm in the absence of light to give dimethyl disulphide (117 g, 1·25 mol), methyl-*n*-propyl disulphide (183 g, 1·5 mol), and di-*n*-propyl disulphide (166 g, 1·12 mol).

(3) *Methyl*-n-*butyl Disulphide.*—The irradiation of a mixture of dimethyl disulphide (60 g, 0·64 mol) and di-*n*-butyl disulphide (110 g, 0·62 mol) for 12 hr under similar conditions gave on fractionation, in the absence of light, methyl-*n*-butyl disulphide (50 g, 0·37 mol) in addition to the two symmetrical disulphides.

(4) *Methyl*-tert-*butyl Disulphide.*—An equimolar mixture of di-*tert*-butyl disulphide and dimethyl disulphide was irradiated under similar conditions for 16 hr. Fractionation of the product in the absence of light gave no unsymmetrical compound.

(e) *Disproportionation of Unsymmetrical Disulphides by Irradiation*

(1) *Methyl-n-butyl disulphide.*—This disulphide (50 g) was irradiated by means of a 500-watt U.V. lamp for 14 hour. The product was fractionated at a pressure of 17 mm in the absence of light and found to consist of unsymmetrical disulphide and symmetrical disulphides in the molar ratio of 4 : 1.

(2) *Methyl-tert-butyl Disulphide.*—A quantity (200 g) of this disulphide was irradiated for 14 hr by means of a 500-watt U.V. lamp. Careful fractionation of the product, in the absence of light, yielded only the unchanged unsymmetrical compound without any trace of symmetrical compounds. The purity of the material before irradiation was 99·0 per cent and afterwards 97·6 per cent (before fractionation).

(f) *Irradiation in the Presence of Acrylonitrile*

To a 10 ml solution of freshly distilled acrylonitrile (4 vol) in 40° to 60° C petroleum ether (5 vol) in a transparent silica or pyrex tube was added approximately 0·005 mol of the disulphide. The solution was boiled to remove dissolved oxygen, cooled in an atmosphere of nitrogen or carbon dioxide, tightly corked, and exposed to the source of light together with a similar sample containing no disulphide. When comparative tests were being made the samples were stored in the dark until all were prepared and then exposed simultaneously. It was found that on storage many of the disulphide samples decomposed with the formation of free sulphur (or polysulphides), and it was essential to ensure that samples were free from either of these compounds which inhibited the formation of the macropolymer. The following modification of the doctor test was employed to test their freedom from sulphur or polysulphide :—

The disulphide (1 ml) was added to a very dilute solution of the corresponding mercaptan in 40° to 60° C petroleum ether (3 ml). Sodium plumbite solution (3 ml) was added, and the mixture was shaken for 30 sec. If no precipitate formed at the interface or no discoloration of the petroleum layer took place within 30 min the sample was free from sulphur or polysulphides.

(g) 1 : 2-*Diathan* (1 : 2-*Dithiacyclohexane*)

Butane-1 : 4-dithiol was prepared by the method described [41] for the preparation of ethane-1 : 2-dithiol. It had the following physical constants : b.p. 87·5° C at 21 mm; f.p. −52·064° C, purity 99·88 mol per cent; n_D^{20} 1·5298; n_D^{25} 1·5273; d^{20} 1·0433; d^{25} 1·0392. The dithiol (61 g, 0·5 mol) was dissolved in *n*-pentane (600 ml) and added to an aqueous solution (600 ml) of potassium iodide (10 g) in a separating funnel which was painted to exclude light. Iodine (127 g, 1 g atm) was added in small portions with vigorous shaking and cooling. The aqueous layer was separated off and the pentane solutions washed with water until neutral, then with sodium thiosulphate solution, and finally with water. It was filtered, cooled to −60° C and the mother liquors decanted from the solid which separated. This process was repeated twice with fresh *n*-pentane and the solid freed from solvent *in vacuo* at 0° C in the dark. The yield was 55 g, 92 per cent theoretical, m.p. 30—42° C, purity 99·8 mol per cent, b.p. 186° C at 760 mm, 25° C at 1·6 mm. This compound has been prepared previously

from the alkyl dithiosulphate by Affleck and Dougherty,[42] who obtained a 20 per cent yield of a liquid product. Our compound could be stored without change at 0° C in the dark, but on exposure to light it changed into a polymeric material; the change was more rapid when the compound was in the liquid state. There appeared to be two forms of polymer—a solid form which on distillation at atmospheric pressure in the dark depolymerized to the monomeric form and a rubbery form which would not depolymerize.

Acknowledgment

The authors thank the chairman of the Anglo-Iranian Oil Company Ltd. for permission to publish these results and V. E. Gripp for assistance in some of the irradiation experiments.

References

1 Birch, S. F., and Stansfield, R. *Industr. Engng Chem.* (*Industr.*), 1936, **28**, 668.
2 Ryan, J. G. *Industr. Engng Chem.* (*Industr.*), 1942, **34**, 824.
3 McAllan, D. T., Cullum, T. V., Dean, R. A., and Fidler, F. A. *J. Amer. chem. Soc.*, 1951, **73**, 3627.
4 Kleiman, M. U.S.P. 2,474,849, 5.7.49.
5 Rheinboldt, H., and Motzkus, E. *Ber.*, 1939, **72**, 657.
6 Kolthoff, I. M., and Harris, W. E. *Analyt. Chem.*, 1949, **21**, 963.
7 Proell, W. A. U.S.P. 2,521,870, 12.9.50.
8 Proell, W. A. U.S.P. 2,557,312, 19.6.51.
9 Kleiman, M. U.S.P. 2,510,893, 6.6.50.
10 Kleiman, M. U.S.P. 2,510,894, 6.6.50.
11 Kharasch, M. S., Nudenburg, W., and Mantell, G. J. *J. org. Chem.*, 1951, **16**, 524.
12 Maruin, J., and Pâris, R. *Compt. rend.*, 1950, **231**, 1297.
13 Michaelis, L., and Schubert, M. P. *Chem. Rev.*, 1938, **22**, 437.
14 Foss. O. *Acta chem. scand.*, 1950, **4**, 404.
15 Claesson, —. *J. prakt. Chem.*, 1877, [2], **15**, 214.
16 Holmberg, B. *Ann.*, 1908, **359**, 81.
17 Tasker, H. S., and Jones, H. O. *J. chem. Soc.*, 1909, **95**, 1910.
18 Claesson, —. *J. prakt. Chem.*, 1877, [2], **15**, 193.
19 Holmberg, B. *Ber.*, 1910, **43**, 220.
20 Riding, R. W., and Thomas, J. S. *J. chem. Soc.*, 1923, **123**, 3271.
21 Strecker, W. *Ber.*, 1908, **41**, 1105.
22 Mann, F. G., Pope, W. J., and Vernon, R. H. *J. chem. Soc.*, 1921, **119**, 634.
23 Patel, P. D., Sen-Gupta, J., and Chakravarti, G. C. *J. Indian Inst. Sci.*, 1930, **13***A*, 73.
24 Schulze, W. A., Short, G. H., and Crouch, W. W. *Industr. Engng Chem.* (*Industr.*), 1950, **42**, 916.
25 Olin, J. F. U.S.P. 2,237,627, 8.4.41.
26 Lyon, J. P., and Crouch, W. W. U.S.P. 2,527,948, 31.10.50.
27 Schulze, W. A., and Crouch, W. W. U.S.P. 2,529,355, 7.11.50.
28 Rule, A., and Thomas, J. S. *J. chem. Soc.*, 1914, **105**, 2819.
29 Baxendale, J. H., Evans, M. G., and Park, G. S. *Trans. Faraday Soc.*, 1945, **42**, 155.
30 Gorin, G., Dougherty, G., and Tobolsky, A. V. *J. Amer. chem. Soc.*, 1949, **71**, 3551.
31 Lecher, H. *Ber.*, 1915, **48**, 524.
32 Schönberg, A., and Mustafa, A. *J. Amer. chem. Soc.*, 1951, **73**, 2401.
33 Schönberg, A., Mustafa, A., and Askar, W. *Science*, 1949, **109**, 522.
34 Schönberg, A., Rupp, E., and Gumlich, W. *Ber.*, 1933, **66***B*, 1932.
35 Cutforth, G. H., and Selwood, P. W. *J. Amer. chem. Soc.*, 1948, **70**, 278.
36 Eby, L. T. Division of Organic Chemistry of the American Chemical Society, 118th National Meeting, Chicago, Ill., Sept. 1950.
37 Skerret, N. P., and Thompson, N. W. *Trans. Faraday Soc.*, 1941, **37**, 81.
38 Kharasch, M. S., and Fuchs, C. F. *J. org. Chem.*, 1948, **13**, 97.
39 Franklin, J. L., and Lumpkin, H. E. *J. Amer. chem. Soc.*, 1952, **74**, 1023.
40 Arnold, R. C., Lien, A. P., and Alm, R. M. *J. Amer. chem. Soc.*, 1950, **72**, 731.
41 Cope, A. C. "Organic Syntheses," Vol. 30, John Wiley and Sons Inc., New York, 1950, p. 35.
42 Affleck, J. G., and Dougherty, G. *J. org. Chem.*, 1950, **15**, 865.

THE ISOMERIC THIOPHTHENS AND THEIR ETHYL HOMOLOGUES. THE ORIENTATION OF DERIVATIVES OF LIQUID THIOPHTHEN (THIOPHENO–2′ : 3′ : 2 : 3–THIOPHEN)

By Frederick Challenger * (Fellow) and Brian Fishwick *

Summary

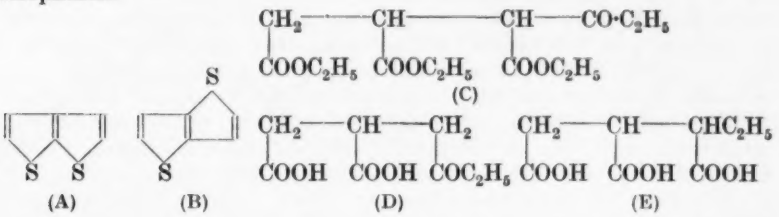
An extensive study of substitution in solid (or *S*-) thiophthen and in liquid (or *L*-) thiophthen has been carried out. It is known that electrophilic substituents, including the $-COCH_3$ group, enter the same position in the solid and also in the liquid isomer. The methyl ketones of the two thiophthens have been reduced by the Wolff–Kishner method to the corresponding ethylthiophthens, which have been characterized by the preparation of numerous derivatives. In the case of ethyl-*L*-thiophthen these derivatives are identical with those obtained from a specimen of 2-ethyl-*L*-thiophthen synthesized from β-carboxy-δ-oxo-*n*-heptoic acid and phosphorus trisulphide. They were found to be different from those of the 3-ethyl-*L*-thiophthen obtained from α-ethyltricarballylic acid and phosphorus trisulphide. Electrophilic substituents therefore enter the molecule of *L*-thiophthen in the 2- or α-position where the sulphur atom occupies position 1.

Several derivatives of ethyl-*S*-thiophthen have been prepared.

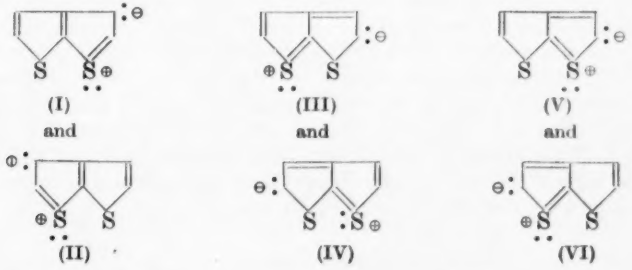
The liquid isomer of thiophthen, (A) thiopheno-2′ : 3′ : 2 : 3-thiophen was first prepared by Biedermann and Jacobson [1] by heating citric acid or tricarballylic acid with phosphorus trisulphide. See also Oster.[2] Hanna and Smith [3] obtained the same compound from aconitic acid and the trisulphide. Challenger and Harrison [4] isolated liquid thiophthen and also a solid isomer (B) from the products of the interaction of acetylene and boiling sulphur. X-ray photographs and the zero dipole moment [4] established the structure (B) for the solid isomer, a conclusion confirmed by the extensive X-ray studies of Cox, Gillott, and Jeffrey.[5] It was therefore clear that the thiophthen obtained by Capelle [6] from acetylene and sulphur must have been a mixture. The identity of the liquid thiophthen prepared from citric acid with that obtained from acetylene and sulphur was at first in doubt,[4] but was conclusively established by Challenger and Emmott,[7] who employed a method due to Challenger, Clapham, and Emmott [8] for detecting the presence of traces of the solid isomer (thiopheno-2′ : 3′ : 3 : 2-thiophen) in the liquid thiophthen. Following the notation employed in previous communications the liquid isomer (A) is designated *L*-thiophthen and the solid (B) as *S*-thiophthen. It was established [7,8] that the common electrophilic groups, *e.g.*, CH_3CO-, $-NO_2$, $-MgBr$, and $-I$ enter the molecule of *L*-thiophthen in the same position and that this, with the addition of the $-HgO{\cdot}COCH_3$ residue, is also true for the solid isomer.[9] The position of entry was, however, not decided, but the results now to be described prove that in *L*-thiophthen this is the 2- or α-position. J. L. Holmes (forthcoming publication) has recently shown that

* Department of Organic Chemistry, The University, Leeds.

electrophilic substituents also enter the position α- to sulphur in solid thiophthen.



Reduction of methyl-*L*-thiophthienyl ketone (-acetothiophthienone) $CH_3CO{\cdot}C_6H_3S_2$ by the Clemmensen or the Wolff–Kishner [11] reaction gives a liquid ethyl-*L*-thiophthen from which several derivatives have been prepared and shown to be identical by m.p. and mixed m.p. determinations with the corresponding derivatives of the 2-ethyl-*L*-thiophthen synthesized from β-carboxy-δ-oxo-*n*-heptoic acid (D) $EtCOCH_2{\cdot}CH(COOH){\cdot}CH_2COOH$. The derivatives in question are the 1 : 3 : 5-trinitrobenzene compound, the picrate, the nitro-compound, and the methyl ketone (methyl ethyl-*L*-thiophthienyl ketone), its semicarbazone, and its oxime. All these compounds, however, differ in m.p. from the corresponding derivatives of 3-ethyl-*L*-thiophthen prepared from α-ethyltricarballylic acid (E) $COOH{\cdot}CHEt{\cdot}CH(COOH){\cdot}CH_2COOH$ and phosphorus trisulphide. The mixed m.p. showed considerable depressions in each case. It is clear, therefore, that substitution takes place in the 2-position, and this is in accordance with what would be expected from the effect of the unshared electrons of the two sulphur atoms. This effect was originally discussed for the case of thiophen by Schomaker and Pauling.[10] The following resonance structures yielding a negative charge on the carbon atoms should contribute to some extent to the structure of liquid thiophthen and control substitution by electrophilic reagents



As four structures produce a negative charge in the α- or 2-position compared with only two structures producing a negative charge in the β- or 3-position, the excited state of the molecule with a negative charge on C-atom 2 may be expected to have a lower energy, and therefore to be more stable than the excited state where the negative charge is on C-atom 3. Electrophilic substitution should therefore take place in an α- or 2-position.

In order to determine the most suitable conditions for the reduction of

L-acetothiophthienone to ethyl-*L*-thiophthen, a preliminary study was made of the relative merits of the Clemmensen and Wolff–Kishner [11] methods of reduction. The corresponding methyl-*S*-thiophthienyl ketone was employed for this purpose, as it was available in much larger quantities. In one case the Wolff–Kishner reaction, using the semicarbazone and fused potassium hydroxide, yielded some solid thiophthen in addition to the ethyl-*S*-thiophthen. No benzene was detected, however, when the same conditions were applied to the reduction of acetophenone semicarbazone, acetophenone azine and ethylbenzene being the products. The modified Wolff–Kishner method employing hydrazine hydrate and potassium hydroxide in diethylene glycol [12] was found to be preferable to the Clemmensen method, which, owing to the use of hot strong hydrochloric acid, caused much resinification of the thiophthen.

Ethyl-*S*-thiophthen is a liquid, and was characterized by the preparation of the 1 : 3 : 5-trinitrobenzene derivative, the nitro-compound, the methyl ketone, and its semicarbazone and oxime. Attempts to prepare ethyl-*S*-thiophthen by the Friedel–Crafts reaction using alkyl-halides with stannic, zinc, or aluminium halides were unsuccessful.

The preparation of β-carboxy-δ-oxo-*n*-heptoic acid (D) started from ethyl propioacetate, which was prepared by the method of Willstätter and Clark.[13] This was then condensed with ethyl fumarate to give ethyl α-propiotricarballylate (C), by the procedure described by Ruhemann and Browning [14] for the α-aceto-derivative. Hydrolysis and elimination of carbon dioxide gave the keto-acid (D). α-Ethyltricarballylic acid (E) was prepared by the method of Ruhemann and Cunnington [15] from diethyl ethylmalonate, sodium ethoxide, and ethyl fumarate; hydrolysis and decarboxylation of the resulting tetracarboxylic ester gave the required acid. Slight modifications of the original method were found necessary. Complete hydrolysis was not accompanied by complete decarboxylation, and it was found necessary to heat the mixture of tri- and tetra-carboxylic acids to 180° to ensure this. The resulting ethyltricarballylic acid was, as pointed out by Michael,[16] a mixture of two racemic forms which were not completely separable by crystallization, nor was this necessary for the purpose. The highest m.p. reached was 148·5°, whereas Michael [16] and Jowett [17] give 156° to 157°. Auwers, Köbner, and v. Meyenburg,[18] who prepared the acid by the method used by the present authors, record a m.p. of 147° to 148°. Acid of m.p. 144° to 147°, or even as low as 130°, was used for the reaction with phosphorus trisulphide. The chemical purity of the acid of m.p. 144° to 145° was checked by analysis and determination of equivalent. The tri-*p*-bromophenacyl ester was also prepared.

Experimental

Preparation of L-*Thiophthen from Citric Acid and Phosphorus Trisulphide.*

This preparation was carried out by the method of Challenger and Harrison [4] (see also Challenger, Clapham, and Emmott [8]). The *L*-thiophthen was purified as before by formation of its picrate in methyl alcohol. The m.p. was 137°, unchanged on recrystallization. The picrate was mixed with sodium carbonate, and the liberated *L*-thiophthen distilled in steam, extracted with ligroin, dried over calcium chloride, the solvent

removed, and the oil distilled, giving *L*-thiophthen, b.p. 100·5° to 101·5°/16 mm.

The 1 : 3 : 5-*Trinitrobenzene Derivatives of the Thiophthens.* The 1 : 3 : 5-trinitrobenzene derivative of *L*-thiophthen. 1 : 3 : 5-Trinitrobenzene (0·35 g) was added to *L*-thiophthen (0·23 g). The mixture was recrystallized from methyl alcohol when its m.p. was found to be constant at 141·5° to 142°. The derivative was a yellow crystalline solid. (Found: C, 40·7; H, 2·0; N, 11·8; S, 18·1. $C_{12}H_7O_6N_3S_2$ requires C, 40·8; H, 2·0; N, 11·9; S, 18·1 per cent.)

The 1 : 3 : 5-*Trinitrobenzene Derivative of* S-*Thiophthen.* This was prepared in a similar way as a yellow solid which was recrystallized from methyl alcohol to a constant m.p. of 148·5° to 149·5°. (Found: C, 41·0; H, 2·0; N, 11·9; S, 17·9. $C_{12}H_7O_6N_3S_2$ requires C, 40·8; H, 2·0; N, 11·9; S, 18·1 per cent.)

Synthesis and Properties of 3-*Ethyl*-L-*thiophthen*

Preparation of n-*Pentane-*α,β,γ,γ-*tetraethylcarboxylate.* This was prepared by the Michael reaction between diethyl fumarate and diethyl ethylmalonate, according to Ruhemann and Cunnington's method.[15]

A mixture in molar proportions of diethyl ethylmalonate (200 g) and diethyl fumarate (180 g) was added to sodium ethoxide (10·5 g) dried at 180° in a reflux apparatus under a calcium chloride tube and warmed on the steam bath for 7 hours. After cooling, dilute sulphuric acid was added. The reddish oily layer was extracted with ether. The oil so obtained yielded unchanged esters of b.p. below 110°/16·5 mm (50 g), and *n*-pentane-α, β, γ, γ-tetraethylcarboxylate (300 g) which distilled at 207° to 210°/20 mm. The yield was 79 per cent. This reaction was repeated four times. Altogether 875 g of diethyl fumarate and 960 g of diethyl ethylmalonate gave 1362 g of *n*-pentane-α, β, γ, γ-tetraethylcarboxylate. Yield 74 per cent. (Found: C, 56·35; H, 7·5. Calc for $C_{19}H_{28}O_8$: C, 56·65; H, 7·8 per cent.)

Preparation of α-*Ethyltricarballylic Acid by Hydrolysis and Decarboxylation of* n-*Pentane-*α, β γ, γ-*tetraethylcarboxylate.* The method of Michael was employed. *n*-Pentane-α, β, γ, γ-tetraethylcarboxylate (160 g) was heated under reflux with water (160 cc) and hydrochloric acid (160 cc) for 72 hours (a few hours longer than the time required for the solution to become completely clear). The solution was concentrated and hydrogen chloride removed by repeated evaporation with small quantities of water, finally giving 92 g of a very thick syrup, which solidified overnight. In order to complete the decarboxylation (which was only partial during the boiling with hydrochloric acid) the solid was kept at 180° till evolution of carbon dioxide ceased (1 hour). The acid residue was dissolved in water and evaporated to a thick syrup which solidified overnight. After recrystallizing four times from acetone–benzene the m.p. was constant at 144° to 145°. Yield 40 g.

A further 19 g of m.p. about 130° was isolated from the mother liquors. The m.p. of the acid could not be raised above 145° by solution in hot glacial acetic acid and leaving below 0° for several days. When recrystallized several times from acetone–benzene the m.p. was 148·5°, but could be raised no further. A specimen was analysed. (Found: C, 46·8; H, 5·9. Calc for $C_8H_{12}O_6$: C, 47·1; H, 5·9 per cent.)

Proof that the Acid m.p. 144° to 145° *is Chemically Pure* α-*Ethyltricarb-*

allylic Acid. (1) *Analysis.* The acid m.p. 144° to 145° gave similar results on analysis. (Found : C, 47·0; H, 6·1. Calc for $C_8H_{12}O_6$: C, 47·1; H, 5·9 per cent.)

(2) The equivalent weight of the acid was determined : (*a*) by analysis of the silver salt and (*b*) by titration. (Found : 69·70; (*b*) 67·5, 68. Calc for $C_8H_{12}O_6$: 68.)

A total of 303 g of this acid, m.p. 144° to 145°, was obtained from 1300 g of *n*-pentane-α, β, γ, γ-tetraethylcarboxylate. This represented a yield of 41 per cent. In addition, 164 g of the acid with a lower melting point was isolated from the acetone–benzene mother liquors. Neither an amide nor an anilide of the acid could be prepared; the *p*-nitrobenzyl ester solidified in a freezing mixture, but liquefied at room temperature.

The p-*Bromophenacyl Ester.* To a neutral solution of the sodium salt of α-ethyltricarballylic acid (0·2 g) *p*-bromophenacyl bromide (1 g) and alcohol (10 cc) was added. The mixture was heated at 100° for 4 hours, then allowed to cool. A white solid separated (0·36 g), m.p. 144° to 145°. The ester was recrystallized from aqueous acetone to a constant m.p. of 145·5°. (Found : C, 48·3; H, 3·55; Br, 29·8. $C_{32}H_{27}O_9Br_3$ requires C, 48·3; H, 3·4; Br, 30·15 per cent.)

Two attempts to prepare the *S*-benzyl*iso*thiouronium salt gave a product which was recrystallized many times, but no consistent melting point could be obtained.

Preparation of 3-*Ethyl*-L-*thiophthen from* α-*Ethyltricarballylic Acid and Phosphorus Trisulphide.* The apparatus was similar to that used for the preparation of *L*-thiophthen (p. 222), but a smaller reaction flask (250 cc) was used, and two caustic soda traps and two picric acid traps were placed in series with the receiver. Two experiments were carried out with an intimate mixture of α-ethyltricarballylic acid (10 g), phosphorus trisulphide (15 g), and sulphur (1 g) and seven with double these quantities. The mixture was heated slowly in an oil bath. At about 160° a fairly violent reaction took place and some reddish oil collected in the first receiver. Heating was continued to 280°, during which time a few more drops of oil distilled. The distillate in the sodium hydroxide traps was extracted, sometimes without distillation in steam, with 40° to 60° ligroin, yielding after drying a deep reddish oil (7·3 g).

The yield of crude 3-ethyl-*L*-thiophthen was about 7 per cent. On distillation under reduced pressure, a small fraction collected below 120°/15 mm. The main fraction distilled at 120° to 122°/13 mm. This was redistilled.

Attempted Purification of the Crude Oil by Means of its Picrate. The calculated weight of picric acid in warm methyl alcohol was added to the oil. On cooling, much picric acid separated. The mother liquor gave an orange-coloured picrate, m.p. 40° to 45°, which could not be recrystallized owing to its solubility. The 3-ethyl-*L*-thiophthen was therefore recovered by addition of sodium carbonate and steam distillation, giving pure 3-*ethyl*-L-*thiophthen* (2 g) in a yield of 2·5 per cent. (Found : C, 57·15; H, 5·2; S, 37·95. $C_8H_8S_2$ requires C, 57·1; H, 4·8; S, 38·1 per cent.) Although the result for hydrogen is slightly high, there is no doubt that the product was 3-ethyl-*L*-thiophthen.

Attempts to Find a Suitable Derivative for the Purification of 3-*Ethyl*-L-*thiophthen.* To each of the following compounds a drop of 3-ethyl-*L*-

thiophthen was added: 2 : 4 : 6-trinitrotoluene, 2 : 4 : 6–2′ : 4′ : 6′-hexanitrodiphenylamine, 1 : 2 : 4-trinitrobenzene, 1-chloro-2 : 4-dinitrobenzene, 1-chloro-3 : 4 : 6-trinitrobenzene, 1-chloro-2 : 4 : 6-trinitrobenzene, 2 : 4 : 6–2′ : 4′ : 6′-hexanitrohydrazobenzene, 1 : 3 : 5-trinitrobenzene. In none of the first seven cases was any evidence of reaction observed. With 1 : 3 : 5-trinitrobenzene, however, reaction occurred.

1 : 3 : 5-*Trinitrobenzene Derivative of* 3-*Ethyl*-L-*thiophthen*. 3-Ethyl-*L*-thiophthen (0·10 g) and 1 : 3 : 5-trinitrobenzene (0·13 g) gave a deep yellow product which was crystallized twice from a little hot methyl alcohol when the m.p. was constant at 81° to 81·5°. (Found: C, 44·1; H, 2·9; N, 11·1; S, 17·3. $C_{14}H_{11}O_6N_3S_2$ requires: C, 44·1; H, 2·9; N, 11·0; S, 16·8 per cent.) The product was obviously an addition compound of 3-ethyl-*L*-thiophthen and 1 : 3 : 5-trinitrobenzene in molecular proportions. The analysis of another specimen of this compound in which the value for the sulphur content was found to agree almost exactly with the theoretical is given below. Regeneration of the ethylthiophthen from this derivative could not be successfully accomplished by steam distillation alone, as some trinitrobenzene volatilized. On steam distillation with 2N-sodium hydroxide, a pure 3-ethyl-*L*-thiophthen was obtained. This treatment was later applied to all the analogous trinitrobenzene derivatives, but unfortunately the trinitrobenzene cannot be recovered.

Preparation of 3-*Ethyl*-L-*thiophthen from α-Ethyltricarballylic Acid of Lower Melting Point* (p. 222). Crude 3-ethyl-*L*-thiophthen was prepared from this sample of acid (165 g), by the method previously described. A pale yellow oil (6·55 g) was obtained in a yield of 4·8 per cent, and was purified as before through the trinitrobenzene derivative, m.p. 81°. The pure 3-ethyl-*L*-thiophthen obtained in all previous preparations was combined (7·0 g). It distilled at 130° to 134°/20 mm as a clear colourless oil; 5·9 g. Yield, 2·4 per cent. (Found: C, 57·3; H, 5·0; S, 37·9. $C_8H_8S_2$ requires C, 57·1; H, 4·8; S, 38·1 per cent.)

Derivatives of 3-*Ethyl*-L-*thiophthen*. The 1 : 3 : 5-trinitrobenzene derivative was prepared as described above, m.p. 81° to 81·5°. (Found: C, 44·0; H, 3·1; N, 11·1; S, 16·9. $C_{14}H_{11}O_6N_3S_2$ requires C, 44·1; H, 2·9; N, 11·0; S, 16·8 per cent.)

Nitro-3-*Ethyl*-L-*thiophthen*. The method of preparation was similar to that used for nitro-*L*-thiophthen. A solution of 3-ethyl-*L*-thiophthen (1 g) in acetic anhydride (0·6 to 0·7 cc) was cooled in ice and salt. The nitrating mixture of fuming nitric acid (0·33 cc) in acetic anhydride (3·3 cc), which had also been cooled in the freezing mixture was slowly added, over a period of about 15 minutes. The mixture was then left in ice and salt for a further 10 minutes and became dark green in colour. The mixture was next poured into iced water containing sodium bicarbonate (10 g), giving a sticky reddish-orange mass which was distilled in steam. An orange oil containing unchanged 3-ethyl-*L*-thiophthen was obtained in the first 200 cc of distillate. A voluminous pale yellow solid (0·27 g), m.p. 64° to 67°, collected in the next litre, representing a yield of 21 per cent. The low yield was mainly due to the formation of a non-volatile black substance. The yellow solid when recrystallized from ethyl alcohol had m.p. 68·5°. (Found: C, 45·2; H, 3·3; N, 6·65; S, 29·8. $C_8H_7O_2NS_2$ requires C, 45·05; H, 3·3; N, 6·6; S, 30·1 per cent.)

Preparation of 3-*Ethyl*-L-*acetothiophthienone*. The method used was similar to that described by Challenger and Harrison [4] for the preparation of *L*-acetothiophthienone. Stannic chloride (2·5 g) in carbon disulphide (8 cc) was treated drop by drop with 3-ethyl-*L*-thiophthen (1 g) and acetyl chloride (1 g) in carbon disulphide (8 cc) with shaking during about 10 minutes. The mixture became red, then purple, and finally black. It was then left overnight.

Iced water was added, the solvent removed, and the mixture distilled in steam, giving a white emulsion which was extracted with ether and dried over sodium sulphate, finally yielding a brown oil (0·78 g) in a yield of 62 per cent. A black substance, presumed to be a polymer, was left in the reaction flask.

The oil deposited a solid after standing about two days in the refrigerator. This was drained on tile and recrystallized from aqueous alcohol to m.p. 50° to 51°. When the tile was extracted with ether, more crystals were obtained from the oil. The total weight was about 0·2 g, corresponding to a yield of 15 per cent.

After as much solid, m.p. 50·5°, as possible had been isolated from the oil, two unsuccessful attempts were made to isolate another isomer by washing the oil with solvents and freezing. In a second preparation the reaction mixture was heated for 2 to 3 hours. The weight of pure ketone obtained was 0·68 g; yield 27 per cent. Thus, the yield appeared to be slightly improved by heating and by the use of larger quantities. (Found : C, 56·9; H, 5·0; S, 30·5. $C_{10}H_{10}OS_2$ requires C, 57·1; H, 4·8; S, 30·5 per cent.)

3-*Ethyl*-L-*acetothiophthienone* 2 : 4-*Dinitrophenylhydrazone*. The 2 : 4-dinitrophenylhydrazone of the ketone sintered from about 190° to 195°, and could not be purified owing to insolubility in all common solvents.

3-*Ethyl*-L-*acetothiophthienone Semicarbazone*. 3-Ethyl-*L*-acetothiophthienone (0·1 g) in alcohol was added to semicarbazide hydrochloride (0·1 g) and sodium acetate (0·15 g) in water. The mixture was left for several days, but no solid separated. On warming for 1 hour a yellow precipitate formed. Next day this was boiled with ethyl alcohol, thereby removing much insoluble material of m.p. about 250° (*d*). Addition of water to the solution gave a white solid; this, when recrystallized from aqueous alcohol, had the constant m.p. of 224·5° (*d*). (Found : C, 49·7; H, 5·3; N, 15·6; S, 23·8. $C_{11}H_{13}ON_3S_2$ requires C, 49·4; H, 4·9; N, 15·7; S, 24·0 per cent.)

3-*Ethyl*-L-*acetothiophthienone oxime*. 3-Ethyl-*L*-acetothiophthienone (0·1 g), hydroxylamine hydrochloride (0·1 g), and barium carbonate (0·1 g) were warmed under reflux with alcohol (2 to 3 cc), for 5 hours, filtered, and the residue washed with small amounts of hot alcohol. The solution yielded a white solid which was thoroughly extracted with ether, finally giving an oil which soon solidified. When recrystallized from aqueous alcohol the m.p. was 103·5°. (Found : C, 53·1; H, 5·0; N, 6·2; S, 28·4. $C_{10}H_{11}ONS_2$ requires C, 53·3; H, 4·9; N, 6·2; S, 28·45 per cent.)

Preparation of Ethyl-S-*thiophthen by Reduction of* S-*Acetothiophthienone*.

Preparation of Ethyl-S-*thiophthen by Reduction of* S-*Acetothiophthienone by the Clemmensen Method*. The method of Challenger and Harrison [4] for the preparation of ethyl-*S*-thiophthen was followed. Zinc wool (25 g) was

washed three times with hot dilute hydrochloric acid. The mercuric chloride (2 g), hydrochloric acid (1·25 cc), and water (35 cc) were added and shaken for 15 minutes. The liquid was decanted and the zinc amalgam well washed with water. *S*-Acetothiophthienone (4 g), water (75 cc), and hydrochloric acid (75 cc) were then added and the mixture heated under reflux for 12 hours. After each period of 3 hours an extra 12 cc of hydrochloric acid was added.

Extraction with ether and drying over calcium chloride and removal of the ether left a brown, oily solid. This was extracted with 40° to 60° ligroin, leaving a tar which was not further investigated, being assumed to be a polymer of ethyl-*S*-thiophthen. The ligroin yielded a viscous oil, from which further extraction with ligroin removed an orange oil. This was distilled at 14 mm, giving a colourless oil; 0·12 g. Assuming this to be ethyl-*S*-thiophthen, it represented a yield of 3 per cent theoretical.

Further Preparation of Ethyl-S-thiophthen by the Clemmensen Method. A modification of this method was then used. To the zinc amalgam (6 g) was added *S*-acetothiophthienone (1 g), water (18 cc), and hydrochloric acid (18 cc). The mixture was heated under reflux for 2 hours, when all the *S*-acetothiophthienone appeared to have been reduced. The mixture was then distilled in steam, yielding a trace of oil. This was extracted, dried, and distilled as before, giving 0·09 g of oil representing a yield of ethyl-*S*-thiophthen of 10 per cent. With a longer reaction period (4 hours) the yield was also 10 per cent.

The product was identified as ethyl-*S*-thiophthen by analysis of its 1 : 3 : 5-trinitrobenzene derivative. The oil (0·18 g) and 1 : 3 : 5-trinitrobenzene (0·23 g) were dissolved in warm methyl alcohol. On cooling, a yellow solid, m.p. 84° to 86°, was obtained. It was recrystallized from methyl alcohol to a constant melting point of 86°. (Found: C, 44·1; H, 3·0; N, 10·9; S, 16·85. $C_{14}H_{11}O_6N_3S_2$ requires C, 44·1; H. 2·9; N, 11·0; S, 16·8 per cent.)

Effect of the Conditions during the Clemmensen Reduction on the Thiophthen Nucleus. *S*-Thiophthen (2 g) was heated under reflux with zinc amalgam and dilute hydrochloric acid (1 : 1) for 5 to 6 hours. Hydrogen sulphide could be detected by smell and by lead acetate paper. The mixture was then distilled in steam. A black, non-volatile residue remained; this was probably a polymer or decomposition product of *S*-thiophthen. The distillate yielded unchanged thiophthen (0·8 g), m.p. and mixed m.p. 55°. It is obvious that *S*-thiophthen is unstable under the conditions of the Clemmensen reduction.

Attempts to Prepare Ethyl-S-thiophthen by a Friedel–Crafts Reaction between S-Thiophthen and an Ethyl Halide. With ethyl bromide or iodide and stannic chloride or ethyl iodide and zinc chloride, all in carbon disulphide, most of the thiophthen was recovered unchanged; with ethyl bromide and aluminium chloride in the same solvent much polymerization occurred. No ethylthiophthen was obtained in any of these experiments.

Preparation of Ethyl-S-thiophthen from S-Acetothiophthienone by the Kishner Method of Reduction. The ketone (2 g), semicarbazide hydrochloride (5 g), and sodium acetate (7 g) in water (50 cc) and alcohol (100 cc) were warmed until clear. A thick white precipitate formed overnight. This was separated and dried (2·3 g); yield 88 per cent. It was impossible

to purify the semicarbazone owing to its insolubility. The crude semicarbazone (2·3 g) and solid potassium hydroxide (3 g) were heated in an oil bath. The mixture darkened above 100° and gradually fused. At 180° ammonia was evolved. The mixture was maintained at 200° to 220° for 15 minutes. When frothing had ceased the pressure was reduced to 14 mm. An oil–water mixture distilled below 200°.

The distillate was extracted with light petroleum, finally yielding a yellow oil (0·6 g), which was treated with 1 : 3 : 5-trinitrobenzene (0·8 g) in methyl alcohol. The product, after four crystallizations from methyl alcohol, had m.p. 149° and showed no depression of m.p. on mixing with the 1 : 3 : 5-trinitrobenzene derivative of *S*-thiophthen, m.p. 148·5° to 149·5°. (Found : C, 40·8; H, 2·0; N, 12·1; S, 18·2. $C_{12}H_7O_6N_3S_2$ requires C, 40·8; H, 2·0; N, 11·9; S, 18·1 per cent.) Thus, it appeared that some thiophthen had been produced during the Kishner reduction. The mother liquors from the first two recrystallizations were concentrated, giving a yellow solid, m.p. 82° to 83°. After six recrystallizations from methyl alcohol this had m.p. 85·5°. A mixed m.p. with an authentic specimen of the 1 : 3 : 5-*trinitrobenzene derivative of ethyl*-S-*thiophthen* gave no depression, thus establishing the identity of the compound, a conclusion confirmed by analysis. (Found : C, 44·4; H, 3·0; N, 10·8; S, 16·8. $C_{14}H_{11}O_6N_3S_2$ requires C, 44·1; H, 2·9; N, 11·0; S, 16·8 per cent.)

In another experiment the semicarbazone was heated under reflux with solid potassium hydroxide (3 g). After 5 hours the mixture was red in colour and ammonia was still being evolved. The mixture was then fused over a flame and distilled in steam, yielding a yellow oil (0·9 g). This with picric acid, gave the picrate of ethyl-*S*-thiophthen which, after three crystallizations from methyl alcohol, had m.p. 72·5° to 73° (0·8 g). (Found : C, 41·8; H, 2·9; N, 10·8; S, 16·6. $C_{14}H_{11}O_7N_3S_2$ requires C, 42·3; H, 2·8; N, 10·6; S, 16·1 per cent.) No *S*-thiophthen picrate could be obtained from the mother liquors, which were concentrated, mixed with sodium carbonate, and distilled in steam. The volatile oil (0·3 g) was extracted with ligroin and identified by conversion to the 1 : 3 : 5-trinitrobenzene derivative of ethyl-*S*-thiophthen, m.p. 85·5° to 86°.

Effect of the Kishner Reduction Method on Acetophenone. The semicarbazone of acetophenone was mixed with potassium hydroxide (15 g) and heated in an oil bath to 220°. The mixture partially fused, and a colourless liquid distilled during 5 to 6 hours. The oil (2·5 g) was separated from the aqueous distillate, dried, and on redistillation this had b.p. 135° to 136° and consisted of ethylbenzene (1·2 g). No benzene could be detected. The residue in the distilling flask deposited a yellow solid, which on recrystallization from ethyl alcohol melted at 121° to 122°. (Found : C, 80·8; H, 6·8; N, 11·7 per cent. Mol wt 224. $C_{16}H_{16}N_2$ requires C, 81·3; H, 6·8; N, 11·9 per cent. Mol wt 236.) The compound did not depress the m.p. of authentic acetophenoneazine, m.p. 121·5 to 122° (Ferguson and Goodwin [19]; Blout, Eager, and Gofstein [20]).

Preparation of Ethyl-S-thiophthen by Reduction of S-Acetothiophthienone by the Modified Wolff–Kishner Method. The method followed in this preparation was Lon's modification of the Wolff–Kishner method.[12]

Potassium hydroxide (0·5 g), 90 per cent hydrazine hydrate (0·5 cc), diethylene glycol (10 cc), and *S*-acetothiophthienone (1 g) were heated at

110° for 1 hour. The ketone did not dissolve, but slowly fused and blackened. Then a white solid formed and gradually increased as the temperature rose and then slowly disappeared, the mixture becoming reddish-brown in colour. The temperature was then raised to 200° during 1 hour and kept at 200° to 205° for 5 hours. Water and a yellow oil distilled which were later added to the steam distillate.

The cooled mixture was distilled in steam and the distillate extracted with ligroin, yielding a pale yellow oil (0·65 g). The product from two such preparations was combined (2 to 3 g). Distillation gave a clear colourless oil, b.p. 126° to 129°/20 mm (1·9 g), representing a yield of ethyl-*S*-thiophthen of 55 per cent. (Found : C, 57·0; H, 4·95; S, 37·8. $C_8H_8S_2$ requires C, 57·1; H, 4·8; S, 38·1 per cent.)

The 1 : 3 : 5-*Trinitrobenzene Derivative of the Ethyl*-S-*thiophthen obtaine from the Wolff–Kishner Reduction.* Ethyl-*S*-thiophthen (0·2 g) was mixed with 1 : 3 : 5-trinitrobenzene (0·24 g). The derivative melted at 85·5° to 87° and on recrystallization from methyl alcohol at 85·5 to 86·5°. (Found : C, 44·5; H, 3·05; N, 11·2; S, 16·5. $C_{14}H_{11}O_6N_3S_2$ requires C, 44·1; H, 2·9; N, 11·0; S, 16·8 per cent.) This compound was identical with the 1 : 3 : 5-trinitrobenzene derivatives of ethyl-*S*-thiophthen obtained by the Clemmensen (m.p. 85°) or by the Kishner reduction of *S*-acetothiophthienone, m.p. 85·5° (p. 228).

Derivatives of Ethyl-S-*thiophthen*

Nitroethyl-S-*thiophthen.* The method used was similar to that used for nitroethyl-*L*-thiophthen (p. 231). Ethyl-*S*-thiophthen (0·4 g), with a little urea, was dissolved in acetic anhydride (0·3 cc) and the mixture cooled in ice and salt. A cooled mixture of fuming nitric acid (0·1 cc) and acetic anhydride (1 cc) was slowly added. The mixture was left for 10 minutes and then poured into iced water containing sodium bicarbonate.

Distillation in steam gave a brown oil which was extracted with ether, yielding an oil (0·1 g) which partially solidified below 0°. The solid was drained on tile and recrystallized from aqueous alcohol as brownish-yellow leaves, m.p. 93°, insufficient for further recrystallization or for analysis. Most of the ethyl-*S*-thiophthen had formed a black tar.

Ethyl-S-*acetothiophthienone.* The method was similar to that used for the preparation of ethyl-*L*-acetothiophthienone (p. 231). Ethyl-*S*-thiophthen (1 g) and acetyl chloride (1 g) in carbon disulphide (10 cc) were slowly added, with shaking, to stannic chloride (2 g) in carbon disulphide (10 cc), in absence of moisture, and left overnight. The solvent was removed and the residue distilled in steam, giving a white solid (0·86 g; 70 per cent yield), m.p. 66° to 67° and at 72·5° when recrystallized from aqueous alcohol. (Found : C, 57·5; H, 5·15; S, 29·7. $C_{10}H_{10}OS_2$ requires C, 57·1; H, 4·8; S, 30·5 per cent.)

Ethyl-S-*acetothiophthienone Semicarbazone.* The ketone (0·2 g) was added to semicarbazide hydrochloride (0·2 g) and sodium acetate (0·3 g) in aqueous alcohol. After several days a yellowish solid formed. This semicarbazone crystallized from aqueous alcohol and had m.p. 241° (decomp) constant. (Found : C, 50·1; H, 5·0; N, 16·1; S, 24·4. $C_{11}H_{13}ON_3S_2$ requires C, 49·4; H, 4·9; N, 15·7; S, 24·0 per cent.)

Ethyl-S-*acetothiophthienone oxime.* The ketone (0·2 g), hydroxylamine

hydrochloride (0·2 g), and barium carbonate (0·2 g) in alcohol (5 cc) were refluxed for 6 hours. The mixture was filtered, evaporated, and the residue extracted with ether.

The resulting oxime, m.p. 179°, was recrystallized from aqueous alcohol (charcoal), m.p. 182·5° to 183°. (Found : C, 53·5; H, 5·0; N, 6·1; S, 28·2. $C_{10}H_{14}ONS_2$ requires C, 53·3; H, 4·9; N, 6·2; S, 28·45 per cent.)

*The Properties of Ethyl-*L*-thiophthen and its Preparation from* L*-Thiophthen*

The Isolation of Pure L*-Thiophthen from the Crude Product obtained by the Reaction between Sulphur and Acetylene.* The crude oil used consisted of various fractions, b.p. 90° to 120°/10 to 20 mm, from which most of the solid thiophthen had been removed by freezing and all the contaminant, which gives a black mercurated polymer with mercuric chloride. However, this crude oil still contained some solid thiophthen and thionaphthen.

The method of purification adopted followed closely the improved method due to Challenger, Clapham, and Emmott.[8] The *L*-thiophthen, so purified, was subjected to the polymerization test (Challenger, Clapham, and Emmott [8]) for the detection of *S*-thiophthen. To two drops of *L*-thiophthen was added ten drops of a saturated solution of hydrogen bromide in glacial acetic acid. A red solution, which showed no trace of any green colour on standing, was obtained. The precipitated solid was slightly pink in colour. The product was therefore completely free from *S*-thiophthen. The b.p. was 105° to 106°/18 mm.

The Preparation of L*-Acetothiophthienone.* The method used was similar to that of Challenger and Harrison[4] and to that employed for the preparation of *S*-acetothiophthienone.

The quantities were *L*-thiophthen (3·3 g), acetyl chloride (3·3 g), in carbon disulphide (30 cc); stannic chloride (7 g) in carbon disulphide (30 cc). The preparation was carried out three times. The yields were 79, 94, and 84 per cent. The pure *L*-acetothiophthienone had m.p. 114° (Challenger and Harrison [4]). (Found : C, 52·8; H, 3·5; S, 35·1. Calc for $C_8H_6OS_2$: C, 52·7; H, 3·3; S, 35·2 per cent.)

*Preparation of Ethyl-*L*-thiophthen by Reduction of* L*-Acetothiophthienone by the Clemmensen Method.* *L*-Acetothiophthienone was added to zinc amalgam (2·2 g), water (40 cc), and hydrochloric acid (40 cc). The mixture was boiled for 5 hours, and distilled in steam. The distillate was extracted with 40° to 60° ligroin, finally yielding a pale yellow oil (0·7 g) having a characteristic odour, similar to that of ethyl-*S*-thiophthen. Yield 35 per cent. 1 : 3 : 5-Trinitrobenzene (0·9 g) was added to the oil (0·7 g) and the product crystallized three times from methyl alcohol, giving a yellow derivative (1·25 g), m.p. 79·5° to 80·5°. (Found : C, 44·2; H, 3·2; N, 11·0; S, 16·5. $C_{14}H_{11}O_6N_3S_2$ requires C, 44·1; H, 2·9; N, 11·0; S, 16·8 per cent.)

The *trinitrobenzene derivative* (1·1 g) was decomposed by sodium hydroxide solution and distilled in steam. Extraction of the distillate with 40° to 60° ligroin yielded a slightly yellow oil (0·4 g). This was distilled at 16 mm pressure. The b.p. was not determined accurately. (Found : C, 57·1; H, 5·1; S, 38·0. $C_8H_8S_2$ requires C, 57·1; H, 4·8; S, 38·1 per cent.)

*Preparation of Ethyl-*L*-thiophthen by Reduction of* L*-Acetothiophthienone by the Modified Wolff–Kishner Method.* The method was similar

to that used in the preparation of ethyl-*S*-thiophthen (p. 228). Potassium hydroxide (5 g) and 90 per cent hydrazine hydrate (5 cc) were dissolved in diethylene glycol (50 cc). *L*-Acetothiophthienone (6·3 g) was added and the mixture heated in a bath at 100° to 120° for 1 hour, during which time the hydrazone formed. The temperature was then raised to 200° during 30 minutes and maintained at 190° to 200° for 4 hours. A mixture of oil and water, which was later added to the steam distillate, came over. Next day the mixture was distilled in steam. The distillate was extracted with 40° to 60° ligroin, which finally yielded a colourless oil (3·8 g) 65 per cent yield, b.p. 127° to 129°/16 mm. (Found : C, 57·6; H, 4·75; S, 38·2. $C_8H_8S_2$ requires C, 57·1; H, 4·8; S, 38·1 per cent.)

*Derivatives of Ethyl-*L*-thiophthen*

The 1 : 3 : 5-*Trinitrobenzene Derivative.* Some of the oil (0·44 g) produced in the last reaction was mixed with 1 : 3 : 5-trinitrobenzene (0·56 g). The resulting yellow derivative was recrystallized three times from methyl alcohol, m.p. 79° to 80°. (Found : C, 44·3; H, 3·0; N, 11·0; S, 17·0. $C_{14}H_{11}O_6N_3S_2$ requires C, 44·1; H, 2·9; N, 11·0; S, 16·8 per cent.) This trinitrobenzene derivative did not depress the m.p. of that (m.p. 79·5° to 80·5°) obtained by the Clemmensen reduction of *L*-acetothiophthienone (p. 230).

*Ethyl-*L*-thiophthen Picrate.* Picric acid (0·34 g) and ethyl-*L*-thiophthen (0·25 g) gave an orange *picrate* which, when crystallized three times from methyl alcohol, had constant m.p. 67·5° to 68·5°. (Found : C, 42·5; H, 2·5; N, 10·6; S, 16·2. $C_{14}H_{11}O_7N_3S_2$ requires C, 42·3; H, 2·8; N, 10·6 S, 16·1 per cent.)

*Preparation of Nitro-ethyl-*L*-thiophthen.* The reaction was carried out as described for nitro-3-ethyl-*L*-thiophthen (see p. 225) using ethyl-*L*-thiophthen (0·5 g), but a small amount of urea was added before the addition of the nitrating mixture. The first portion of the steam distillate contained a brown oil (A), which was isolated as before. Later a small amount of a yellow solid (B), m.p. 86·5° to 88°, came over. It was recrystallized from aqueous ethyl alcohol, m.p. 89·5° to 90°. (A) partially solidified in the refrigerator, and was drained on tile, when it became yellow. It was recrystallized from aqueous alcohol, m.p. 90° to 90·5°. Extraction of the tile with ether yielded a further quantity of the same m.p. (Found : C, 44·7; H, 3·1; N, 6·9; S, 30·4. $C_8H_7O_2NS_2$ requires C, 45·05; H, 3·3; N, 6·6; S, 30·1.)

*Preparation of Ethyl-*L*-acetothiophthienone.* Stannic chloride (2 g) in carbon disulphide (10 cc), under reflux condenser and calcium chloride tube, was slowly treated with a mixture of ethyl-*L*-thiophthen (1 g) and acetyl chloride (1 g) in carbon disulphide (10 cc). The mixture became dark green and was left overnight. The solvent was removed and iced water added. Distillation in steam gave a white solid and a black, non-volatile residue. The white solid (0·57 g) had m.p. 55·5° to 58°, and corresponded to a yield of crude *ethyl-*L*-acetothiophthienone* of 45 per cent. The ketone was boiled with charcoal in alcohol and crystallized on dilution of the filtered solution with water. It had the constant m.p. of 60° on recrystallization. (Found : C, 57·0; H, 4·9; S, 30·6. $C_{10}H_{10}OS_2$ requires C, 57·1; H, 4·8; S, 30·5 per cent.)

Ethyl-L-*acetothiophthienone semicarbazone.* Ethyl-*L*-acetothiophthienone (0·2 g) was added to semicarbazide hydrochloride (0·2 g) and sodium acetate (0·3 g) in aqueous alcohol, and the clear solution was warmed for 30 minutes, left overnight, and the crystalline precipitate separated and extracted with hot alcohol. Water was added to the extract, and the resulting deposit recrystallized from aqueous ethyl alcohol, m.p. 243°. (Found : C, 49·7; H, 4·9; N, 15·7; S, 23·9. $C_{11}H_{13}ON_3S_2$ requires C, 49·4; H, 4·9; N, 15·7; S, 24·0 per cent.)

Ethyl-L-*acetothiophthienone oxime.* Ethyl-*L*-acetothiophthienone (0·1 g) hydroxylamine hydrochloride (0·1 g), barium carbonate (0·2 g), and ethyl alcohol (2 cc) were refluxed for 6 hours, filtered, and the residue washed with hot alcohol, which was added to the filtrate and the whole evaporated to dryness. Ether extraction yielded a white solid, which was recrystallized from aqueous alcohol, m.p. 171° to 171·5°. (Found : C, 53·3; H, 5·1; N, 6·45; S, 28·9. $C_{10}H_{11}ONS_2$ requires C, 53·3; H, 4·9; N, 6·2; S, 28·45 per cent.)

Synthesis of 2-*Ethyl*-L-*thiophthen*

Preparation of Ethyl Propioacetate. The method was based on that described by Willstätter and Clarke.[13]

Magnesium turnings (11·0 g) and ethyl iodide (72 g) in dry ether (240 cc) were warmed for 30 minutes, cooled, and ethyl cyanoacetate (20 g) in dry ether (24 cc) added drop by drop with stirring. Vigorous reaction took place, and a white precipitate formed, the mixture becoming dark green and viscous. The mixture was then left for 42 hours and just sufficient diluted hydrochloric acid (1 : 1) added to dissolve the magnesium. The yellow ether layer was separated, washed with sodium bicarbonate solution, dried over anhydrous magnesium sulphate, and the ether removed, leaving a dark red oil. On distillation, three main fractions were obtained : (1) b.p. 75·5° to 80·5°/11 mm, 5·8 g corresponding to a yield of 23 per cent of ethyl propioacetate; (2) 80·5 to 96°/11 mm, 3·8 g; (3) 96° to 100°/10 m, 2·6 g.

The b.p. of the third fraction agreed with that of the ketimine corresponding to ethyl propioacetate (Breckpot[21]). It contained nitrogen, and was initially soluble in cold dilute hydrochloric acid, but on standing ethyl propioacetate separated. Fractions (1) and (2) were therefore mixed with cold dilute hydrochloric acid and shaken for 2 hours. Extraction with ether and drying as before yielded a colourless oil (8·9 g), which gave a main fraction (7·1 g), b.p. 77° to 79·5°/11 mm. The yield of ethyl propioacetate was 28 per cent, which could have been improved slightly if the ketimine fraction (3) had also been decomposed. In later experiments the reaction mixture was hydrolysed by slowly adding water with stirring, followed by dilute acid (1 : 1), more than sufficient to dissolve the magnesium. The mixture was then vigorously stirred for 3 hours to hydrolyse any ketimine and treated as before. In four experiments, using 100 g of ethyl cyanoacetate in each case, the yields were 55, 53, 56, and 60·5 per cent. The b.p. of the product ranged from 76° to 79°/10 mm to 80·5° to 82·5°/13 mm. Altogether, 350 g of ethyl propioacetate was obtained from 520 g of ethyl cyanoacetate.

Preparation of Triethyl α-propiotricarballylate. The method was similar to that used by Ruhemann and Browning [14] for triethyl α-acetotricarballylate.

Sodium ethoxide (5·1 g) dried at 180° *in vacuo* and sodium dried ether (50 cc) were treated with ethyl propioacetate (10 g) in dry ether (20 cc). The sodium ethoxide dissolved to a clear yellow-brown liquid. To this was added diethyl fumarate (12 g) in dry ether (10 cc). The ether boiled slowly for some time. The mixture was left overnight. Water (50 cc) and 2N-sulphuric acid (37 cc) were then added and the ether layer separated, washed with sodium bicarbonate, and dried over magnesium sulphate, yielding a deep yellow oil, which when distilled gave *triethyl α-propiotricarballylate* (13·4 g) as a clear colourless oil, b.p. 145° to 151°/0·6 mm, yield 61 per cent. On redistillation the b.p. was 149° to 153°/0·8 mm. (Found : C, 56·9; H, 7·5. $C_{15}H_{24}O_7$ requires C, 57·0; H, 7·6 per cent.)

Preparation of Triethyl α-Propiotricarballylate using a Smaller Amount of Catalyst. The quantities were : sodium ethoxide (1·5 g) in ether (50 cc); ethyl propioacetate (20·2 g) in ether (30 cc), and diethyl fumarate (24 g) in ether (20 cc). All materials were dried. The mixture was left overnight and worked up as before. The main fraction (33·7 g) boiled at 145° to 150·5°/0·5 to 0·6 mm. Yield 76 per cent. Three more preparations under these conditions gave yields of 82, 76, 83 per cent respectively. The b.p. varied between 145° and 152° at 0·5 to 0·7 mm. In all, 560 g of triethyl α-propiotricarballylate was obtained from 320 g of ethyl propioacetate.

The Semicarbazone of Triethyl α-Propiotricarballylate. Triethyl-α-propiotricarballylate (0·5 g), semicarbazide hydrochloride (1 g), and sodium acetate (1·5 g) in aqueous alcohol were left for several days, when white crystals, m.p. 90° to 95°, formed. The *semicarbazone* was recrystallized from warm aqueous alcohol, m.p. 93°. (Found : N, 11·1. $C_{16}H_{27}O_7N_3$ requires N, 11·3 per cent.)

*Preparation of β-Carboxy-δ-oxo-*n*-heptoic Acid.* Triethyl α-propiotricarballylate (100 g), water (250 cc), and hydrochloric acid (250 cc) were boiled under reflux for 18 hours. The clear solution was then evaporated several times with water, finally to dryness and left over potassium hydroxide in a vacuum. The brown residue was dissolved in hot, dry ethyl acetate, filtered hot from insoluble material, and the acid allowed to crystallize, giving 27 g of m.p. *ca* 104° to 105°. Further crystallization of a portion raised the m.p. to 107° to 107·5°. (Found : C, 50·9; H, 6·4. $C_8H_{12}O_5$ requires C, 51·05; H, 6·4 per cent.) The equivalent was determined by titration with sodium hydroxide using phenolphthalein. (Found : 93·2, 93·1. Calc 94·1.)

In all, 506 g of triethyl α-propiotricarballylate gave 160 g of the keto-acid in an overall yield of 53 per cent theoretical. The bulk of the *β-carboxy-δ-oxo-*n*-heptoic acid* (m.p. about 105°) was shown to be pure enough for use in the reaction with phosphorus trisulphide by (*a*) titration against standard alkali and (*b*) by analysis of its silver salt. (Found by (*a*) 94·3, 94·3; by (*b*) 93·7. $C_8H_{12}O_5$ requires E, 94·1.)

Isolation of the Acid-anhydride from the Mother-liquors. The ethyl acetate mother-liquors were evaporated. Part of the residue was then insoluble in ethyl acetate. When separated and washed it formed a white solid of m.p. 242° to 243° when recrystallized from alcohol–benzene.

This substance was probably the *anhydride of β-carboxy-δ-oxo-*n*-heptoic acid.* (Found : C, 56·2; H, 5·8. $C_8H_{10}O_4$ requires C, 56·5; H, 5·9 per cent.)

*The Semicarbazone of β-Carboxy-δ-oxo-*n*-heptoic Acid.* The acid (0·2 g) was added to aqueous semicarbazide hydrochloride (0·2 g) and sodium acetate (0·3 g). A white precipitate formed at once, and was separated next day. It was sparingly soluble in ethyl alcohol, but when recrystallized from hot water had m.p. 173° to 175°. (Found : C, 44·15; H, 6·1; N, 17·6. $C_9H_{15}O_5N_3$ requires C, 44·1; H, 6·1; N, 17·1 per cent.)

*β-Carboxy-δ-oxo-*n*-heptoic Acid 2 : 4-Dinitrophenylhydrazone and its Diethyl Ester.* 2 : 4-Dinitrophenylhydrazine (0·3 g) was dissolved in concentrated sulphuric acid (0·6 cc) and ethyl alcohol (5 cc). Addition of the keto-acid (0·2 g) in ethyl alcohol (2 cc) gave after several hours an oil, which later set to an orange red solid. It was recrystallized from ethyl alcohol to m.p. 48·5° to 49·5°.

Analysis showed that it was the 2 : 4-*dinitrophenylhydrazone of the keto-acid diethyl ester.* (Found : C, 50·4; H, 5·8; N, 13·4. $C_{18}H_{24}O_8N_4$ requires C, 50·9; H, 5·7; N, 13·2 per cent.)

The required 2 : 4-*dinitrophenylhydrazone* was then prepared without the use of alcohol. 2 : 4-Dinitrophenylhydrazine (0·1 g) in 2N-hydrochloric acid (25 cc) and the keto-acid (0·2 g) were warmed at 100° for 30 minutes. Next day an orange red precipitate had formed and was recrystallized from ethyl alcohol, m.p. 174·5° to 175°. (Found : C, 45·9; H, 4·4; N, 15·3. $C_{14}H_{16}O_8N_4$ requires C, 45·6; H, 4·4; N, 15·2 per cent.)

The p-*Bromophenacyl Ester of β-Carboxy-δ-oxo-*n*-heptoic Acid.* A neutral solution of the sodium salt from the keto-acid (0·2 g) in water (5 cc) was added to *p*-bromophenacyl bromide (0·7 g) in alcohol (7 cc). The mixture was heated for 3 hours and left overnight. The solid was recrystallized several times from aqueous alcohol to m.p. of 106·5° to 107°. (Found : C, 49·4; H, 3·9; Br, 27·8. $C_{24}H_{22}O_7Br_2$ requires C, 49·5; H, 3·8; Br, 27·5 per cent.)

*Preparation of 2-Ethyl-*L*-thiophthen from β-Carboxy-δ-oxo-*n*-heptoic Acid and Phosphorus Trisulphide.* β-Carboxy-δ-oxo-*n*-heptoic acid (20 g) and phosphorus trisulphide (40 g) with a little sulphur were thoroughly mixed and slowly heated in an oil bath connected by a water condenser to three flasks containing aqueous sodium hydroxide. Between 180° and 190° a vigorous reaction took place. A thick brown oil distilled with the fumes. Heating was continued to 280°, yielding a few more drops of oil.

The reaction was repeated nine times with β-carboxy-δ-oxo-*n*-heptoic acid (15 g) and the contents of the traps distilled in steam, giving a yellow oil which was extracted with 40° to 60° ligroin and the extract dried over calcium chloride. In all, 155 g of β-carboxy-δ-oxo-*n*-heptoic acid was converted into 9·72 g of a yellow oil which, from its smell, appeared to be a derivative of thiophthen containing some impurity. This represented a yield of 7 per cent based on the keto-acid.

Purification of the Crude Product by means of its 1 : 3 : 5-Trinitrobenzene Derivative. Crude 2-ethyl-*L*-thiophthen (0·9 g) was mixed with 1 : 3 : 5-trinitrobenzene (1·1 g). The red mixture was dissolved in hot methyl alcohol. On cooling, a yellow derivative, m.p. about 70° to 72°, was obtained. After three crystallizations from ethyl alcohol a yellow crystalline solid (0·67 g), m.p. 78° to 79·5°, was finally obtained. The remainder of the crude 2-ethyl-*L*-thiophthen was similarly treated, giving in all 10·35 g of the pure 1 : 3 : 5-trinitrobenzene derivative of 2-ethyl-*L*-thio-

phthen. To this was added aqueous sodium hydroxide and the mixture distilled in steam, giving an almost colourless oil. After extraction with 40° to 60° ligroin most of this (2·94 g) distilled at 133° to 134·5°/21 mm. Yield 2·1 per cent. (Found: C, 57·0; H, 5·2; S, 38·0. $C_8H_8S_2$ requires C, 57·1; H, 4·8; S, 38·1 per cent.)

Derivatives of 2-*Ethyl*-L-*thiophthen*. *The* 1 : 3 : 5-*Trinitrobenzene Derivative*. 2-Ethyl-*L*-thiophthen (0·2 g) was mixed with 1 : 3 : 5-trinitrobenzene (0·24 g) and the product recrystallized from ethyl alcohol; m.p. 79·5° to 80°. (Found: C, 44·4; H, 3·0; N, 10·8; S, 16·9. $C_{14}H_{11}O_6N_3S_2$ requires C, 44·1; H, 2·9; N, 11·0; S, 16·8 per cent.) This did not depress the m.p. of the corresponding derivative of ethyl-*L*-thiophthen (p. 231).

2-*Ethyl*-L-*thiophthen Picrate*. Picric acid (0·3 g) was added to 2-ethyl-*L*-thiophthen (0·2 g) in methyl alcohol. The picrate was very soluble, but crystallized well on cooling. After further recrystallization the m.p. was 67·5° to 68·5°. (Found: C, 42·7; H, 2·9; N, 10·7; S, 16·3. $C_{14}H_{11}O_7N_3S_2$ requires C, 42·3; H, 2·8; N, 10·6; S, 16·1 per cent.) This derivative did not depress the m.p. of ethyl-*L*-thiophthen picrate (p. 231).

Preparation of Nitro-2-*Ethyl*-L-*thiophthen*. Fuming nitric acid (0·17 cc) in acetic anhydride (1·7 cc) cooled in ice and salt was slowly added to 2-ethyl-*L*-thiophthen (0·5 g) in acetic anhydride (0·33 cc) with a little urea, also kept below 0°. The mixture was left in ice and salt for 30 minutes and then poured into iced water containing sodium bicarbonate (5 g). Next day, distillation in steam gave brownish-yellow crystals (A), m.p. 84° to 85°; a black, non-volatile residue remained.

The whole of the distillate was extracted with ether, yielding a brown oil which partly solidified below 0° and was drained on tile. Recrystallization from aqueous ethyl alcohol gave a yellow solid (B), melting at about 85°. (A) and (B) were combined and recrystallized from aqueous ethyl alcohol, giving a yellow solid, m.p. 90° to 90·5° which did not depress the m.p. of nitro-ethyl-*L*-thiophthen (p. 231). (Found: C, 45·3; H, 3·3. $C_8H_7O_2NS_2$ requires C, 45·05; H, 3·3 per cent.)

2-*Ethyl*-L-*acetothiophthienone*. Stannic chloride (2 g) in carbon disulphide (10 cc) under a reflux condenser and calcium chloride tube was slowly treated with a mixture of 2-ethyl-*L*-thiophthen (1 g) and acetyl chloride (1 g) in carbon disulphide (10 cc). The mixture became green, rapidly darkened, and was left overnight. The carbon disulphide was then distilled and the residue treated with iced water. Distillation in steam gave a white solid and black, non-volatile resin. The white solid, after recrystallization from aqueous ethyl alcohol, had m.p. 61·5° to 62°. Yield 0·34 g, 27 per cent. (Found: C, 57·15; H, 4·8; S, 30·9. $C_{10}H_{10}OS_2$ requires C, 57·1; H, 4·8; S, 30·5 per cent.) This derivative did not depress the m.p. of ethyl-*L*-acetothiophthienone (p. 231).

2-*Ethyl*-L-*acetothiophthienone Semicarbazone*. 2-Ethyl-*L*-acetothiophthienone (0·15 g) was added to aqueous alcoholic semicarbazide hydrochloride (0·15 g) and sodium acetate (0·3 g), and the mixture warmed at 100° for 10 minutes. After a few days a yellowish-white precipitate formed, which was separated and extracted with alcohol. Crystallization from aqueous alcohol gave 2-ethyl-*L*-acetothiophthienone semicarbazone, m.p. 243° (decomp.), which did not depress the m.p. of ethyl-*L*-acetothiophthienone

semicarbazone (p. 232). (Found: C, 50·1; H, 5·0; N, 15·9; S, 24·05. $C_{11}H_{13}ON_3S_2$ requires C, 49·4; H, 4·9; N, 15·7; S, 24·0 per cent.)

2-*Ethyl*-L-*acetothiophthienone Oxime*. 2-Ethyl-*L*-acetothiophthienone (0·1 g), hydroxylamine hydrochloride (0·1 g), and barium carbonate (0·1 g) in ethyl alcohol were refluxed for 6 hours. The hot solution was filtered and the residue washed with hot alcohol. The filtrate was then evaporated and the residue extracted with ether, which yielded an almost white solid, which was recrystallized from aqueous ethyl alcohol, m.p. 170·5° to 171·5°. (Found: C, 53·2; H, 5·3; N, 6·15; S, 28·1. $C_{10}H_{11}ONS_2$ requires C, 53·3; H, 4·9; N, 6·2; S, 28·45 per cent.) It did not depress the m.p. of ethyl-*L*-acetothiophthienone oxime (p. 232).

ACKNOWLEDGMENT

The authors thank Imperial Chemical Industries Ltd. for a grant.

References

1 Biedermann, A., and Jacobson, P. *Ber.*, 1886, **19**, 2445.
2 Oster, H. *Ber.*, 1904, **37**, 3350.
3 Hanna, D. C., and Smith, E. F. *J. Amer. chem. Soc.*, 1899, **21**, 381.
4 Challenger, F., and Harrison, J. B. *J. Inst. Petrol. Techn.*, 1935, **21**, 135.
5 Cox, E. G., Gillott, R. J. J. H., and Jeffrey, G. A. *Acta. Crystallographica*, 1949, **2**, 356.
6 Capelle, G. *Bull. Soc. Chim.*, 1908, **3**, 151.
7 Challenger, F., and Emmott, R. *J. Inst. Petrol.*, 1951, **37**, 396.
8 Challenger, F., Clapham, P. H., and Emmott, R. *J. Inst. Petrol.*, 1948, **34**, 922.
9 Challenger, F., and Gibson, G. M. *J. chem. Soc.*, 1940, 305.
10 Schomaker, V., and Pauling, L. *J. Amer. chem. Soc.*, 1939, **61**, 1769.
11 "Organic Reactions," John Wiley and Sons, 1948, **4**, 378.
12 Lon, H. M. *J. Amer. chem. Soc.*, 1946, **68**, 2487.
13 Willstätter, R., and Clarke, C. H. *Ber.*, 1914, **47**, 298.
14 Ruhemann, S., and Browning, K. C. *J. chem. Soc.*, 1898, **73**, 727.
15 Ruhemann, S., and Cunnington, A. V. *J. chem. Soc.*, 1898, **73**, 1006.
16 Michael, A. *Ber.*, 1900, **33**, 3745.
17 Jowett, H. A. D. *J. chem. Soc.*, 1901, **79**, 1346.
18 Auwers, K., Köbner, E., and v. Meyenburg, F. *Ber.*, 1891, **24**, 2890.
19 Ferguson, L. N., and Goodwin, T. C. *J. Amer. chem. Soc.*, 1949, **71**, 633.
20 Blout, E. R., Eager, V. W., and Gofstein, R. M. *J. Amer. chem. Soc.*, 1946, **68**, 1938.
21 Breckpot, R. *Bull. Soc. Chim. Belg.*, 1923, **32**, 386.

THE NEW STANDARD METHOD FOR THE MEASUREMENT OF THE VISCOSITY OF OILS AND OTHER LIQUIDS IN C.G.S. UNITS

THE Institute of Petroleum is now revising the standard method for determining the kinematic viscosity of liquid. Similar action is being taken by the BSI and by the ASTM. This has become necessary consequent upon the decision to use water at 20° C as the sole calibrating liquid. The absolute viscosity of water at 20·00° C has recently been measured by the National Bureau of Standards, using improved means,[1] and the new value of 0·01002 poise for the coefficient of viscosity of water at 20·00° C instead of the hitherto adopted value of 0·01005 poise is to be used from 1 July 1953.

The use of water at 20·00° C as the sole calibrating liquid, instead of using additional oil standards, or 40 and 60 per cent sucrose solutions of known relative viscosity, ensures high precision because of the high accuracy obtained by the NBS in the measurement of the absolute viscosity of water at 20·00° C, namely 0·010019 poise with a standard deviation of ±0·000003. The new standard method describes a master or secondary viscometer for calibration purposes;[2] in designing the master viscometer account has been taken of an error due to surface tension that occurs when the viscosity of an organic liquid is compared with that of water in U-tubes of normal dimensions. The error due to surface tension differences and the correction for kinetic energy have been reduced to a minimum by constructing the special master viscometer with a capillary of diameter 0·045 cm and of length 40 cm instead of the 7 to 12 cm length of the routine type.

The following table summarizes the precision results obtained by the IP Viscosity Panel in an experimental investigation[3] using the master viscometer.

Order of magnitude of viscosity	No. of steps in calibration	Repeatability, % (one operator, one apparatus)	Reproducibility, % (different operator, different apparatus)
1	1	0·14	0·25
10	2	0·16	0·4
100	3	0·2	0·5
500	4	0·3	0·7
1500	5	0·5	1·5

The Viscosity Panel of Sub-Committee No. 6, Lubricants, now has the task of modifying IP 73/47, Viscosity Index, and IP 71/47, Viscosity (Kinematic) in Absolute Units, consequent upon the change in the agreed basic value for the viscosity of water. In methods involving viscosity measurements made prior to 1 July 1953, it is assumed that the basic value for the kinematic viscosity of water at 20° C is 1·0068 cs (1·005 cp), while on and after 1 July 1953, all results will be based on the value 1·0038 cs (1·002 cp).

Viscosity values obtained by method IP 71/52 will remain correct until 1 July 1953; on and after that date all viscosity values obtained by the old method based on the value 1·0068 cs must be multiplied by 0·997. (If on 1 July 1953, the viscometers are recalibrated on the basis of the new value of 1·0038 cs, there will be no need to use the multiplying factor).

With regard to method IP 73/47, Viscosity Index, although the calculation and reporting remain the same, the Table I has to be modified. Values of H, L, and D must be recalculated, based on the new value of 1·0038 cs for the viscosity of water at 20° C. In general, the effect of using the existing table instead of the modified table will be to reduce the calculated V.I. of an oil, the effect being greatest for a low-viscosity, low-V.I. oil, and the least for a high-viscosity, high-V.I. oil. In no case, however, will the decrease be likely to exceed 1 unit in the V.I. range 0 to 100.

Some examples of possible changes in the table are as follows :—

Cs at 210° F	*H*	*L*	*L* − *H*	(*L* − *H*) existing table
2·00	6·632	8·376	1·744	(1·740)
10·00	89·294	162·868	73·574	(73·316)
70·00	1723·0	5669·7	3946·7	(3934·5)

Further examples of differences to be expected are shown in Tables A, B, and C.

TABLE A

	Present table	Modified table	Present table	Modified table
Kin. visc. at 210° F, cs	2·0		2·0	
„ at 100° F, U cs	8·343		6·620	
H	6·620	6·632	6·620	6·632
L	8·360	8·376	8·360	8·376
L − *H*	1·740	1·744	1·740	1·744
L − *U*	0·017	0·033	1·740	1·756
V.I.	0·977	1·892	100·00	100·70
Difference in V.I.	0·915		0·7	
% Difference in V.I.	93·65		0·7	

TABLE B

	Present table	Modified table	Present table	Modified table
Kin. visc. at 210° F, cs	10·0		10·0	
„ at 100° F, U cs	161·8		89·2	
H	89·178	89·294	89·178	89·294
L	162·494	162·868	162·494	162·868
L − *H*	73·316	73·574	73·316	73·574
L − *U*	0·694	1·068	73·294	73·668
V.I.	0·947	1·452	99·97	100·13
Difference in V.I.	0·505		0·16	
% Difference in V.I.	53·33		0·16	

TABLE C

	Present table	Modified table	Present table	Modified table
Kin. visc. at 210° F, cs	70·0		70·0	
,, at 100° F, U cs	5615		1720	
H	1719·9	1723·0	1719·9	1723·0
L	5654·4	5669·7	5654·4	5669·7
L − *H*	3934·5	3946·7	3934·5	3946·7
L − *U*	39·4	54·7	3934·4	3949·7
V.I.	1·00	1·39	100·0	100·08
Difference in V.I.	0·39		0·08	
% Difference in V.I.	39·0		0·08	

The amendments outlined above are being made to the IP methods, and their publication will be made as early as possible.

Copies of the revised V.I. table as soon as available will be obtainable from the Institute on application.

Redwood viscosity values are unaffected by any change in the agreed value for the viscosity of water, since viscosities are expressed in Redwood seconds, *i.e.*, the actual time of efflux, and are not relative to flow time for water. However, any conversion from Redwood viscosity to c.g.s. units obtained by noting the Redwood viscosity of oils of known c.g.s. viscosity will be modified, since the latter will be based on the new viscosity value for water on and after 1 July 1953.

Some slight modification will be necessary in the conversion table of kinematic viscosity to Redwood No. 1 viscosity on p. 676 in the 12th (1952) edition of "Standard Methods for Testing Petroleum and its Products," but any amendments by employing the factor 0·997 probably come within the experimental error.

The amendments of tables will take some time and will not be available in the 1953 edition, but probably in the 1954 edition.

The Viscosity Panel in the meanwhile intend to re-write the IP 71/52 T method for viscosity determination in the light of recent experience and criticism.

References

[1] For technical details see Swindells, J. F., Coe, J. R., Jr., and Godfrey, T. B. "Absolute viscosity of water at 20° C," *J. Res. nat. Bur. Stand.*, 1952, **48**, 1–31; Research Paper 2779.

[2] IP 71/52T. "Standard Methods for Testing Petroleum and Its Products." Institute of Petroleum, 12th edn, 1952, p. 622.

[3] "Investigations on the determination of kinematic viscosity using IP standard methods." *J. Inst. Petrol.*, 1952, **38**, 428–44.

APPLICATION OF PAPER PARTITION CHROMATOGRAPHY TO PETROLEUM ANALYSIS

By Eugenio Mariani *

The possibility of applying paper partition chromatography to petroleum analysis has been examined. The method, which has been applied to some industrial products,† consists ‡ of dropping a small quantity of the material to be tested through a capillary pipette onto a strip of filter paper (2 to 4 cm wide and 50 cm long) at a distance of about 8 to 10 cm from one end, forming a spot not more than 8 to 10 mm in diameter; the end of the strip is then immersed in a solvent so that the remainder of the strip (with the spot) hangs on the outer side of the bowl. The time required for the solvent to permeate the paper strip varies according to the nature of the solvent, and can normally vary from 1 to 2 hours to as long as to 10 to 12 hours; the solvent will carry with it the various components of the spot, which will be found at different distances from the starting point. In the dried strip the position of some among the components is recognizable at first sight; but it has been found useful for the identification of the individual components to observe the strip in ultra-violet light, as the spots are then seen in different fluorescent colours.

Asphalt, both natural and derived from petroleum, has been tested, and because only a small quantity of material is required, it was dissolved, usually in benzene. By choosing the correct solvent or the solvents in which the strips are dipped, it has been possible to locate the positions of the components of an asphalt (asphaltenes, oils, resins) and to recognize them by their different colour in ultra-violet light. In the case of natural asphalt from Selenizza,¶ the asphaltenes present themselves as a dark spot, the resins as an orange-yellow fluorescence spot, and the oils as a larger and more expanded spot, white or pale yellow (Fig 1).

If solvents like benzene, carbon disulphide, chloroform, trichloroethylene, etc., are used it is impossible to separate the oils from the resins; asphaltenes and oil resins only can be identified. It is notable that, although these liquids are more or less good solvents for asphalts, they rarely remove the asphaltenes from their initial position.

Some solvents are capable of separating the oils from the resins; among the best being a mixture of equal volumes of *n*-butyl alcohol and benzyl alcohol. In this solvent the resins hardly move from their initial position, whereas the oils migrate with the same speed as the solvent. It is, there-

* Istituto di Chimica Applicata ed Industriale della Facoltà d'Ingegneria, Università di Roma.

† Mariani, E. *Industr. saccar. ital.*, 1951, **44**, 234, 245; *Sucr. belge*, 1952, **71**, 373; *Nature, Lond.*, 1951, **168**, 959.

‡ The method reported by Schuldiner, J. A. (*Analyt. Chem.*, 1951, **23**, 1676) for the identification of oil products is actually only a capillary analysis method and not a chromatographic one.

¶ Selenizza asphalt, extracted in CS_2, contains 59·2 per cent asphaltenes, 37·8 per cent oils, and 16 per cent resins.

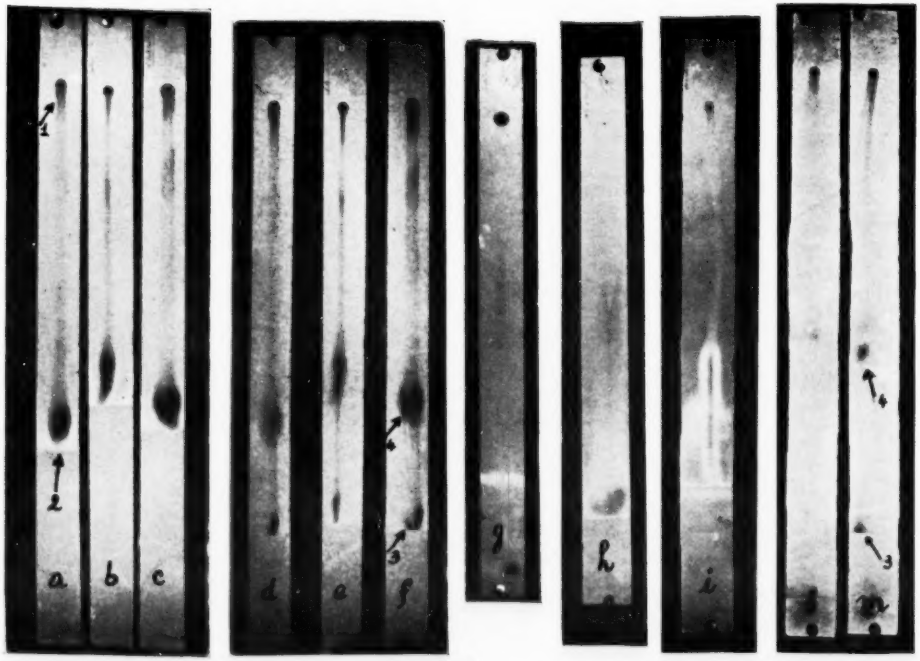


FIG 1

Separation of asphaltenes (1) from oils + resins (2) in *a*: (*a*) petroleum asphalt, (*b*) Selenizza nature asphalt, (*c*) S. Valentino natural asphalt; solvent used, benzene. The chromatograms (*d*), (*e*), and (*f*) are obtained from the preceding strips using, after benzene, another solvent: a mixture (1 : 1 v/v) of butyl and benzyl alcohol. There is evident the separation of oils (3) from resins (4). (*g*) Selenizza nature asphalt chromatographed with acetone. (*h*) and (*i*) show a mixture of oils and resins chromatographed, respectively, with acetone and a mixture of butyl–benzyl alcohol.

(1). (*m*) Asphaltenes after one (*m*) or four (*l*) precipitations; in (*l*) is yet evident a spot due to oils (3) and resins (4).

[*To face p.* 240.

fore, possible to obtain the three groups of substances by the following different methods. The first is a two-dimensional chromatography, the material to be tested being placed on a sheet of filter paper and two solvents (benzene and a mixture of butyl–benzyl alcohol) migrate one after the other in two different directions at right angles. In this way three spots are obtained approximately at the corners of a right-angled triangle. This separation can be more easily performed using a strip of paper, applying the material as usual, dipping in benzene but stopping the run of the solvent when it has progressed to about half the length of the strip and dipping it, after drying, in the second solvent (mixture of two alcohols). This latter liquid will displace neither the asphaltenes nor the resins, but will cause the oils to migrate (Fig 1(*a*), (*b*), (*c*), (*d*), (*e*), (*f*)).

This chromatographic technique has been used to solve an analytical problem. When pure asphaltenes are needed for elementary analysis, molecular weight, etc., it is difficult to ascertain whether or not they still contain any oils and resins.

By carrying out the chromatography of asphaltenes in benzene solution, precipitating them from Selenizza native asphalt in the usual manner, there has been obtained, besides the typical asphaltenes spot, another weak spot due to oils and resins. The asphaltenes have then been redissolved in benzene and reprecipitated twice. After each precipitation a fraction of the product was chromatographed. Fig 1 (*m*), (*l*) reproduces the chromatograms of samples of asphaltenes after the first and fourth precipitations: it will be noticed that the quantity of oils and resins retained by the substance has gradually decreased from one precipitation to another.

This method is also being used for the identification and characterization of crude oils, lubricants, etc.

EMULSIONS OF SEAWATER IN FUEL OIL

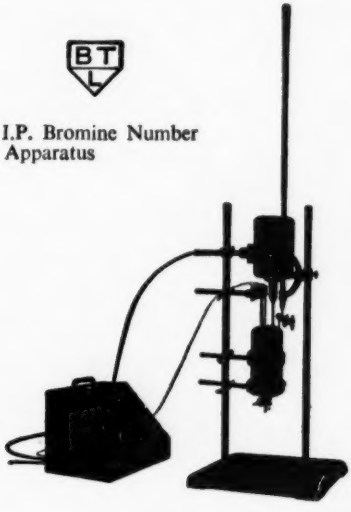
ATTENTION has been directed to the fact that the method of demulsifying seawater–fuel oil emulsions referred to in the paper by W. Killner in the January issue of the *Journal*, is the subject of Patent No. 635,717, the rights of which have been assigned to the National Research Development Corporation.

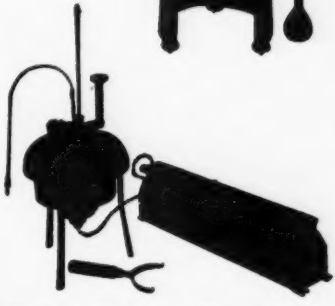
Specialists in the Manufacture of
Laboratory Apparatus for Testing Petroleum Products

I.P. Centrifuge

I.P. Viscometers

I.P. Bromine Number Apparatus





I.P. Flash and Fire Point Apparatus

A full range of apparatus to I.P. specifications

BAIRD & TATLOCK *(LONDON)* **LTD.**

Scientific Instrument Makers

FRESHWATER ROAD, CHADWELL HEATH, ESSEX.

Heat behind bars

KENYON *Planned* HEAT INSULATION

A Shell Photograph

Kenyon provide a *complete* thermal insulation service to the oil industry, including technical advice on thermal insulation specifications, and finishes for all conditions. Supply of materials, application, supervision, on sites throughout the world. The photograph shows columns on the Distillation Unit, M.E.C. project at Ellesmere Port, Cheshire.

Call in KENYON to keep the heat in!

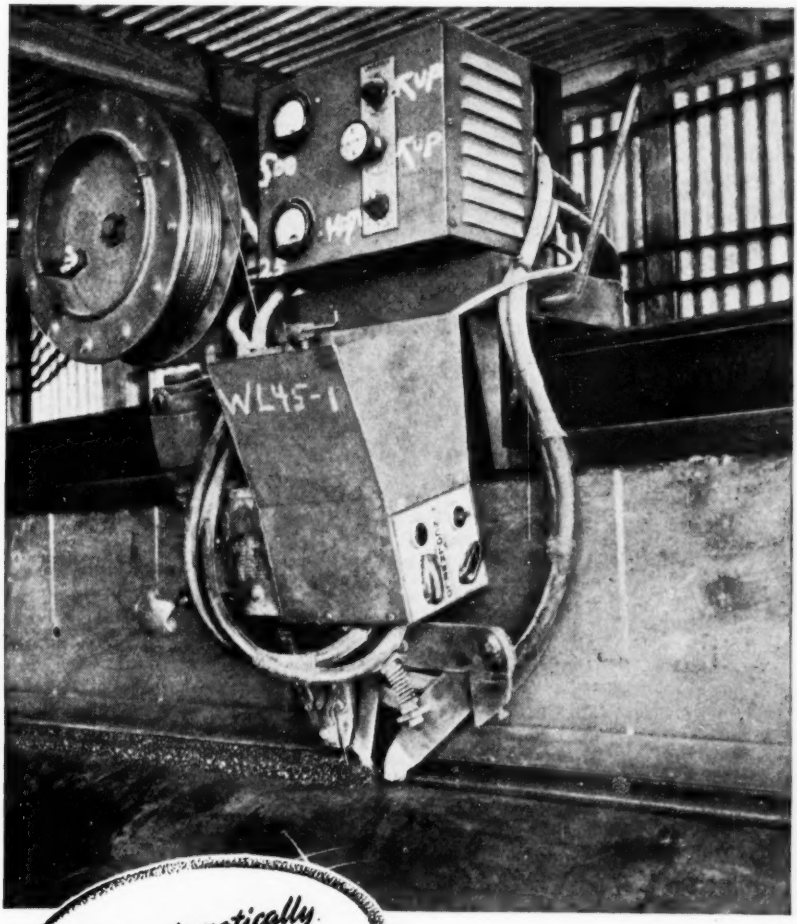
WILLIAM KENYON & SONS LIMITED

DUKINFIELD *Telephone*: ASHTON 1614/7 (4 Lines) **CHESHIRE**

KH 132

Kindly mention this Journal when communicating with Advertisers

Reproduced by kind permission of The Esso Petroleum Co. Ltd.



'We automatically ask Lincoln before we decide'

Lincolnweld Full Automatic equipment was used for seam welding by the Lock Joint Pipe Company in the manufacture of the 30-inch pre-stressed concrete cylinder pipes for the Dominion Republic's water-supply plant at Ciudad Trujillo.

World's largest manufacturers of arc-welding equipment and electrodes

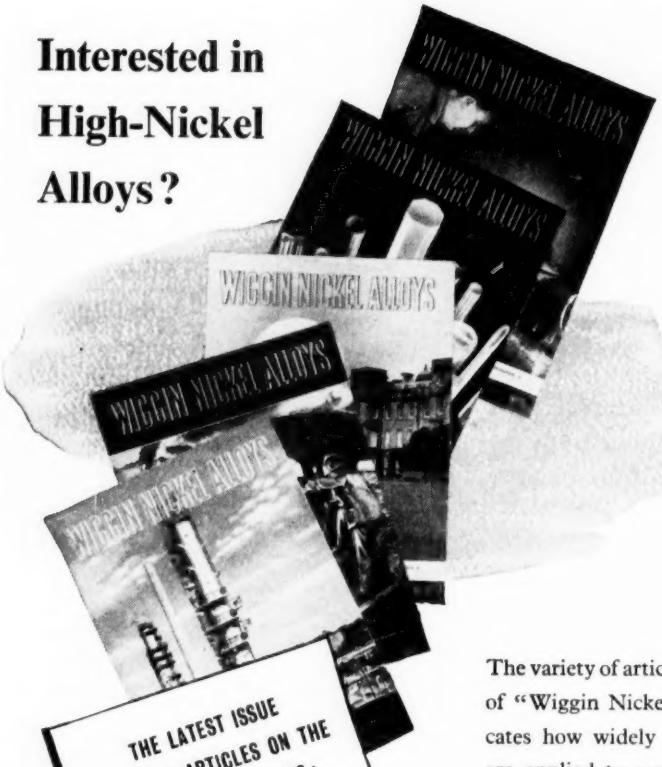
LINCOLN

LINCOLN ELECTRIC CO LTD · WELWYN GARDEN CITY · HERTS · WELWYN GARDEN 920

SM66

36/CR/17

Interested in High-Nickel Alloys?



THE LATEST ISSUE INCLUDES ARTICLES ON THE FOLLOWING SUBJECTS:

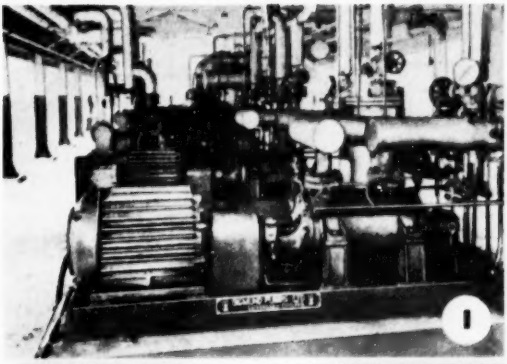
Monel in - - - - - PETROLEUM REFINING PLANT
Monel & K Monel in PUMP UNITS
Nickel Alloys in - - - INDUSTRIAL HEATERS
Monel Bolts in - - - COKE OVEN PLANT
Nimonic Alloys in - - DIESEL ENGINES
Monel Bulbs in - - - RECORDING THERMOMETERS
Nimonic DS for - - - FURNACE BELTS
Nickel in - - - - - - FILLING MACHINES

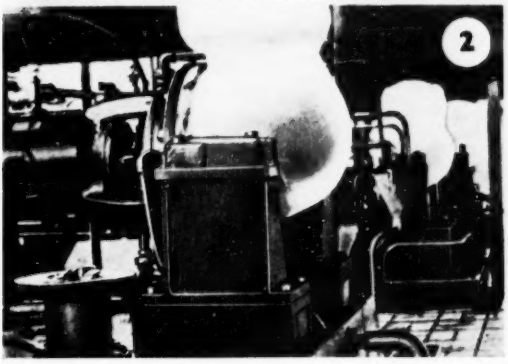
The variety of articles in each issue of "Wiggin Nickel Alloys" indicates how widely these materials are applied to meet difficult and unusual industrial conditions. As the supply position improves, engineers and designers will be able, once more, to take full advantage of the many outstanding properties of the high-nickel alloys.

May we send you a specimen copy?

HENRY WIGGIN & COMPANY LIMITED · WIGGIN STREET · BIRMINGHAM · 16

Performance and Reliability
Proved
in Refineries all over the World





SIGMUND PROCESS PUMPS are taking a leading role in refinery development at home and overseas.

Contracts include:

GREAT BRITAIN

CORYTON, FAWLEY, ELLESMERE PORT, GRANGEMOUTH, ISLE OF GRAIN, SHELLHAVEN, LLANDARCY, STANLOW.

OVERSEAS

BELGIUM, FRANCE, HOLLAND, INDIA, ITALY, INDONESIA, ISRAEL, PERSIA, SOUTH AFRICA, TRINIDAD, VENEZUELA,

and many other refineries and chemical plants.

1. *Multi-stage barrel high temperature pumps (750°F).*
2. *Single-stage HO-N pumps used in sub-zero duties (−32°C) in a de-waxing unit.*

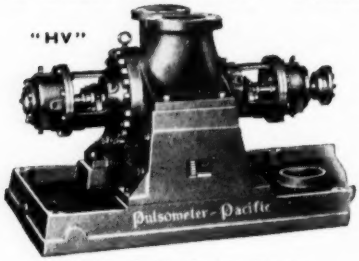
SIGMUND PUMPS LTD.
TERMINAL HOUSE,
GROSVENOR GARDENS,
LONDON, S.W.1

SIGMUND
PROCESS PUMPS

Pulsometer-Pacific

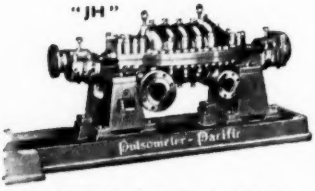
PUMPS FOR THE OIL INDUSTRY

"HV"



Vertically Split Casing Single-Stage Hot Oil Pumps.

"JH"



Horizontally Split Casing Multi-Stage Pumps for Hot Oil.

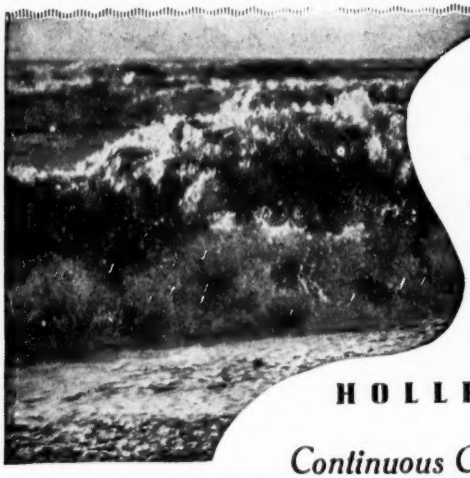
The above are some only of the Designs included.

Established 1875 Advertisement No. 3316

Pulsometer Engineering Co. Ltd.,
Nine Elms Ironworks, Reading.

ENGLAND

CONTINUOUS WASHING



Holley Mott Plants are efficiently and continuously washing millions of gallons of Petroleum products daily. Designed for any capacity. May we submit schemes to suit your needs?

HOLLEY (H M) MOTT

Continuous Counter-Current Plant

Telegrams:
"Typhagitor, Fen, London."
Telephone: Royal 7371/2.

World-Wide Licensees, **H.M. CONTINUOUS PLANT LTD.**
FOUR LLOYDS AVENUE, LONDON, E.C. 3.

THE

MATTHEW HALL

GROUP OF COMPANIES

ESTD. 1848

MATTHEW HALL

OIL REFINERY, CHEMICAL
AND
INDUSTRIAL ENGINEERS

ERECTION OF PLANT
AND MACHINERY
WELDED OIL PIPE LINES
HEATING, AIR CONDITIONING
AND REFRIGERATION
ELECTRICAL FLAMEPROOF
INSTALLATIONS

THE MATTHEW HALL GROUP OF COMPANIES

MATTHEW HALL & CO. LTD. MATTHEW HALL (PTY.) LTD.
KELCO (METALS) LTD. GARCHEY LTD.

LONDON	26-28 Dorset Square, N.W.1	JOHANNESBURG	52 Commissioner Street	DUBLIN	29 Westland Row
MANCHESTER	95-97 Princess Street	GERMISTON	Wadeville	WEST INDIES	Kingston, Jamaica
GLASGOW	85 & 91 Dykebeath Street, S.2	DURBAN	100-103 Williams Road	GIBRALTAR	P.O. Box 306
BELFAST	Greenwood Avenue	CAPE TOWN	Rieboeck Square	SULAWAYO	Abercorn House
		WELKOM	Third Street		

Speedily and without fail Nicerol Foam KILLS petrol and oil fires—and is used by the Royal Navy, Royal Air Force and Oil Companies specifically for that purpose. Nicerol is a concentrate producing a **heavy type of vapour-sealing foam** which flows with creeping flame, blanketing and killing the fire—resisting effectively all possible flash-back or re-ignition. Any type of mechanical or air-foam apparatus will produce foam from Nicerol—either with **fresh** or **salt** water.

Used also by Fire Equipment Manufacturers, Civil Air Lines, Commonwealth and Foreign Governments and Fire Brigades.

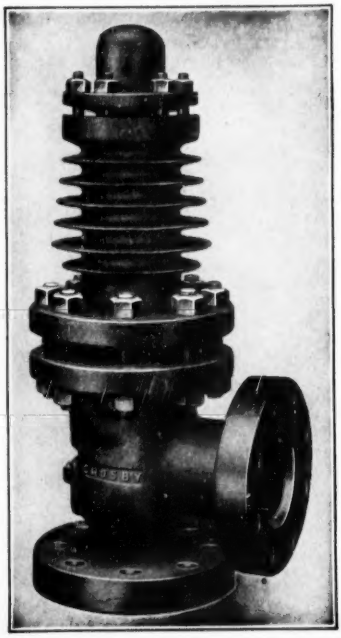
Nicerol is supplied in new heavy gauge steel drums specially designed to permit quick release and clean pouring of contents. These are supplied in 2, 5 or 40 Imperial gallons capacity. 3 gallons of Nicerol will produce over 1,100 gallons of pure white foam.

Sample and illustrated leaflet supplied, with quotation, on request.

NICEROL LIMITED

GREAT BRICK KILN STREET · WOLVERHAMPTON

Tel: WOLVERHAMPTON 24705 *Grams: Nicerol, Wolverhampton*



CROSBY

RELIEF VALVES

FOR OIL REFINERY SERVICE

FOR ALL PRESSURES UP TO 2,700 LBS.
TEMPERATURES UP TO 1,000° F.

MASONEILAN

AUTOMATIC CONTROLS

FOR LEVEL, PRESSURE, ETC.

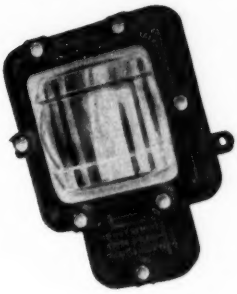
CROSBY VALVE & ENGINEERING CO. LTD.

251, EALING ROAD, WEMBLEY

DORMAN

Flameproof equipment

(BUXTON CERTIFIED)



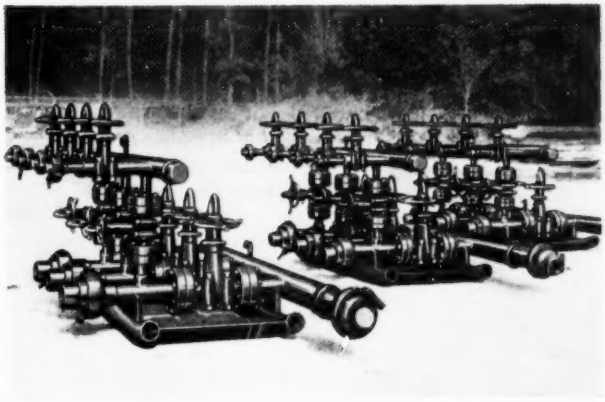
Flameproof prismatic lighting fitting, the DORMAN "DIOPRISM" 100 watt – conforms to requirements of the Ministry of Mines.

4-way S.P. & N. Flameproof switch fuse distribution board —

— with "T" type isolating switch

DORMAN & SMITH LTD. **MANCHESTER 5**

THE BRITISH OILFIELD EQUIPMENT COMPANY LIMITED



hold the sole manufacturing licence for the world-famous—

Cameron

FLEX-SEAL VALVE manufactured at their Works at Leeds and obtainable for payment in Sterling. These valves can be supplied over a range of sizes and pressures either as separate units or assembled in pre-fabricated manifold units as depicted.

Your enquiries are invited

BOFEC

THE BRITISH OILFIELD EQUIPMENT CO. LTD

DUKE'S COURT, 32 DUKE STREET, LONDON, S.W.1 *Tel: Whitehall 6177*

THE SCIENCE OF PETROLEUM

THE WORLD'S OIL FIELDS:

The Eastern Hemisphere

VOLUME VI PART I

Edited by V. C. Illing

This volume has just been published and it reviews the present state of knowledge about the geology of oil in the Eastern Hemisphere. *Published* 52*s.* 6*d. net.*

SYNTHETIC PRODUCTS OF PETROLEUM

VOLUME V PART II

Edited by A. E. Dunstan and B. T. Brooks

This volume covers the synthetic products of petroleum, including raw materials for rubber solvents and refinery processes. *Published* 100*s. net.*

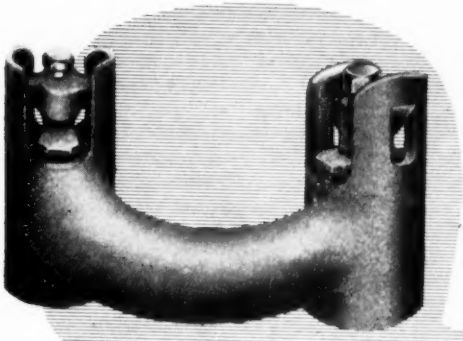
THE SCIENCE OF PETROLEUM consists, so far, of Volumes I, II, III and IV (105*s.* each), published in 1938, and Volume V Part I, *Crude Oils* (48*s.* net), published in 1950. It provides the petroleum world with a continuous exegesis of the developments of its science and technology. *A prospectus giving details is available on application to the publishers:*

OXFORD UNIVERSITY PRESS

Amen House, Warwick Square, London, E.C.4

OSBORN-OHIO

oil refinery fittings



for EXTRA Service Efficiency

TYPE 1000
MULE EAR FITTINGS

This type of fitting lends itself to the *Directional Solidification* principle of casting, which ensures complete soundness without centre-line weakness and shrinkage.

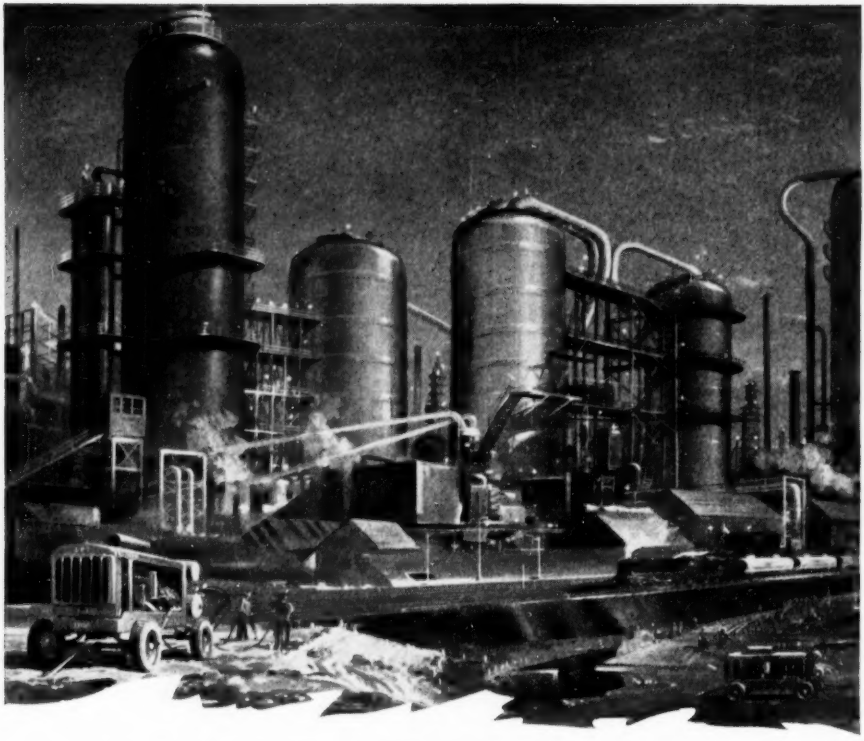
For many years, Osborn Foundry & Engineering Co. Limited, have specialised in the manufacture of Return Bends for Oil Refineries and Chemical Plant. They are cast in many types of steel, for all pipe sizes, are of rugged construction, thoroughly dependable, and will give years of trouble free service.

All Osborn fittings are interchangeable with those made by Ohio Steel Foundry Co., being made in accordance with Ohio designs.

Catalogues will be sent upon request.

OSBORN

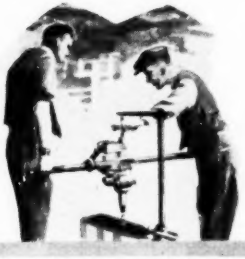
SAMUEL OSBORN & CO. LIMITED
CLYDE STEEL WORKS, SHEFFIELD



SERVING THE PETROLEUM INDUSTRY . . .

Air power has many meanings today . . . but throughout the petroleum industry it is synonymous with Consolidated Pneumatic—the air power that plays a vital role in "Keeping the oil flowing." In construction . . . in maintenance, CP compressors provide that air power with taken-for-granted reliability and efficiency . . . CP tools make the utmost use of every cubic foot of it. And behind both is a vast background of specialised experience . . . a vast chain of depots for advice and service.

FOR THE RIGHT APPROACH . . .
THE RIGHT EQUIPMENT



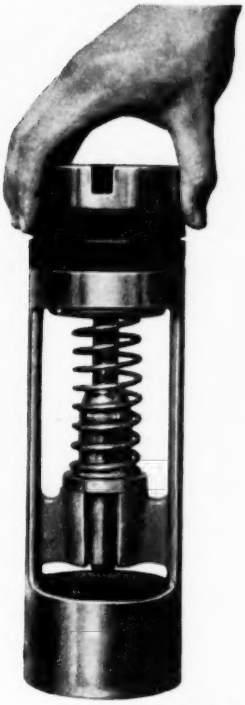
CALL IN CONSOLIDATED

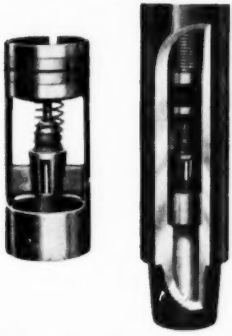
CONSOLIDATED PNEUMATIC TOOL CO. LTD. **LONDON & FRASERBURGH**

Reg. Offices: 232 Dawes Road, London, S.W.6 Offices at Glasgow · Newcastle · Manchester · Birmingham Leeds · Bridgend · Belfast · Dublin · Johannesburg · Bombay · Melbourne · Paris · Rotterdam · Brussels · Milan and principal cities throughout the World

Kindly mention this Journal when communicating with Advertisers

IT PAYS TO "FLOAT" DRILL PIPE





The Valve Assembly is dropped in place by hand and is held there by the tool joint pin above it.

With a BAKER Bakwik Drill Pipe Float

(Product No. 480)

because it brings you these important results:

PREVENTS PLUGGING THE BIT with the hazard and grief of wet strings

RELIEVES WEIGHT ON DERRICK and other rig equipment

LENGTHENS LIFE OF WIRE LINES and brake bands

MINIMIZES OR PREVENTS SERIOUS DAMAGE in event of a parted string

DOES NOT INTERFERE WITH DRILLING or the running of a surveying device

---

NO TROUBLE TO INSTALL OR REMOVE

The Baker BAKWIK Model "B" Drill Pipe Float Valve Assembly is positioned at the desired point in the drilling string, either in the float body or in a valve chamber in the drill collar. The strong, simple valve assembly—made entirely without threads—is dropped into place by hand and held securely in position by the tool joint pin above it. No tools or wrenches are required to install or remove it. When an unrestricted fluid passage way is desired, the BAKWIK Valve Assembly can be removed from the float body, or drill collar, quickly and easily. The Valve Assembly is readily serviced right on the derrick floor, with inexpensive parts which are available from any field shop or warehouse. ● Drilling departments find that this unit gives them extremely low-cost insurance for the important results and the worthwhile savings it provides. ● See the Baker (or Composite) Catalogue for complete details, or write direct to:

BAKER OIL TOOLS, INC.

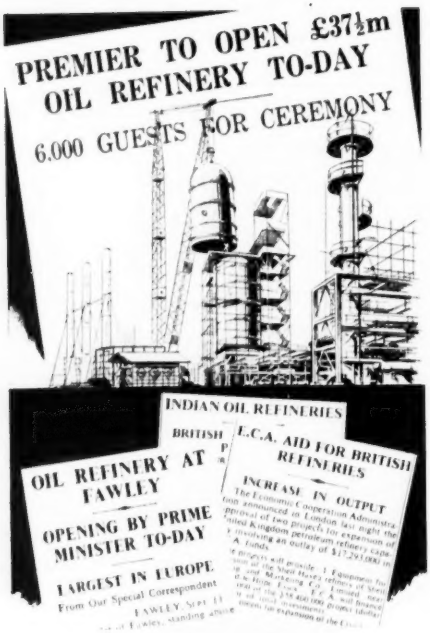
Box 2274 Terminal Annex, Los Angeles 54, California, U.S.A.

Manufactured in England, under license by

THE OIL WELL ENGINEERING CO., LTD.,

Cheadle Heath, Stockport.

BAKER Bakwik DRILL PIPE FLOAT



FOR AN EXPANDING INDUSTRY

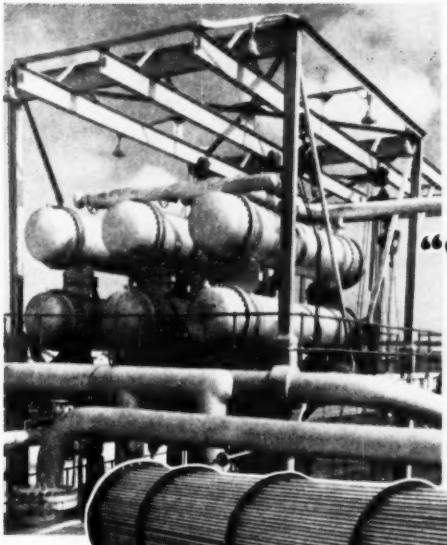
High Quality Brass & Copper Tubes promptly supplied by

John Wilkes, Sons & Mapplebeck Limited

During the rapid growth of Britain's oil refining industry, John Wilkes, Sons & Mapplebeck have kept pace with an increasing demand for brass and copper tubes for all purposes—maintaining the reputation for high quality which they have enjoyed for more than a century.

JOHN WILKES, SONS & MAPPLEBECK LIMITED · BIRMINGHAM 18

WP



"Yorcalbro"
TUBES
FOR
HEAT
EXCHANGERS
AND
CONDENSERS

The
YORKSHIRE COPPER WORKS
LIMITED
LEEDS & BARRHEAD

TYLORS'
"VISUFLO"
METER

combines positive volumetric measure and totalizing with rate of flow indication. Special materials for different types of liquids.

TYLORS OF LONDON LTD
(Established 1777)
BELLE ISLE · YORK WAY · LONDON, N.7
Telegrams: Tylosis, Phone, London Telephone: North 1625

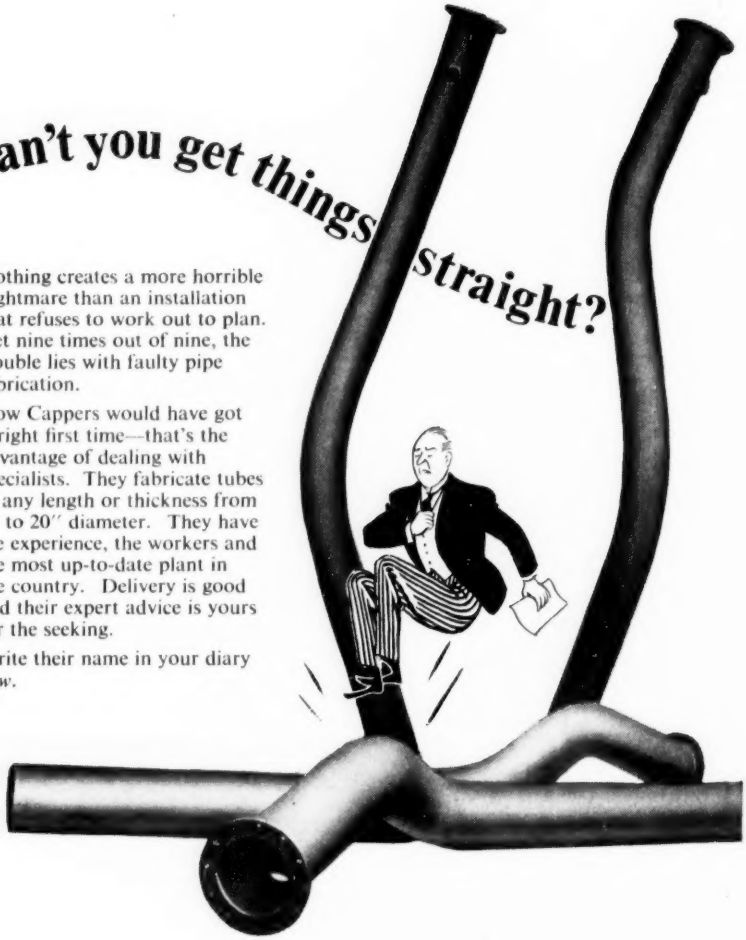
SPECIALISTS IN ALL LIQUID METERING PROBLEMS

Can't you get things straight?

Nothing creates a more horrible nightmare than an installation that refuses to work out to plan. Yet nine times out of nine, the trouble lies with faulty pipe fabrication.

Now Cappers would have got it right first time—that's the advantage of dealing with specialists. They fabricate tubes of any length or thickness from ¼" to 20" diameter. They have the experience, the workers and the most up-to-date plant in the country. Delivery is good and their expert advice is yours for the seeking.

Write their name in your diary *now*.



IF IT'S TUBE FABRICATION CONSULT

CAPPERS

Please write for our catalogue No. 4 which gives the full range of our products

WILLIAM H. CAPPER & CO. LTD., FORWARD WORKS, WOOLSTON, WARRINGTON
Telephone: Warrington 3266/7/8

London Offices: 20 SOUTHAMPTON PLACE, W.C.1. *Telephone: CHAncery* 4721

Kindly mention this Journal when communicating with Advertisers

Quasi-Arc
REG. TRADE MARK

ELECTRODES FOR EVERY ARC WELDING APPLICATION

MILD STEEL

RADIAN (New type)
VORTIC
FERROSPEED
PIPE WELDING
PRESSURE VESSEL
WELDEEP
TWIN-ARC. R

HIGH TENSILE STEELS

LOW HYDROGEN 35
PIPE WELDING (Mo. B)
VORTIC (Mo. B)
ARMOID No. 1
ARMOID No. 2

CORROSION RESISTING STEELS

CHROMOID Nos. 1, 2 & 3
THERMOID Nos. 1, 2 & 3

HARD-SURFACING and MANGANESE STEELS

DUROID Nos. 1, 2 & 3
MANGANOID (New type)
MANGCROSS (New type)

CAST IRON

FERROLOID No. 1
FERROLOID No. 2

NON-FERROUS

ALUMOID No. 2
BRONZOID No. 1
MIRROID

Separate Technical Circulars dealing with each of the above types are available on request

THE QUASI-ARC COMPANY LTD

Bilston · Staffordshire

Telephones: Bilston 41905 (6 lines)

Manufacturers of Electrodes

Plant and Accessories for Electric Arc Welding

QA27A

EDECO
REGD. TRADE MARK
OIL FIELD EQUIPMENT
ROCK BITS, DRILL COLLARS, SUBSTITUTES, DRAG BITS, SWABS, SLUSH PUMP SPARES
JET NOZZLES AVAILABLE OVER THE FULL 10 TYPE RANGE
VS2 JET TYPE
ENGLISH DRILLING EQUIPMENT CO., LTD.
BILBAO HOUSE, 36-38 NEW BROAD STREET, LONDON, E.C.2
Telephone: LONdon Wall 4941-4
Telegrams: Bullwheel, Ave., London
Subsidiary Companies
EDECO PROSPECTORS, LTD. Batley Works, Fixby, Nr. Huddersfield, Yorks. Tel.: Eland 2876/7
EDECO CANADA, LTD. 10103-80th Avenue, Edmonton, Alberta. Tel.: Edmonton 35825
EDECO (TRINIDAD) LTD. P.O. Box 27 San Fernando, Trinidad, B.W.I. Tel.: San Fernando 2819
EDECO DEUTSCHLAND, G.m.b.H. Falschbloock C, Hermannstr. 40, Hamburg 1. Tel.: Hamburg 33, 34, 47

CRAIG

COMPREHENSIVE SERVICE

*

REFINERY DESIGN AND CONSTRUCTION

•

ATMOSPHERIC AND
VACUUM DISTILLATION UNITS

•

COMBINED DISTILLATION,
CRACKING, REFORMING AND
VAPOUR PHASE TREATING UNITS

•

PARAFFIN WAX EXTRACTION,
REFINING AND MOULDING

•

GASOLINE RECOVERY
AND STABILISATION UNITS

•

HEAT EXCHANGE EQUIPMENT OF ALL TYPES

•

FRACTIONATING COLUMNS
AND TUBE STILLS

A. F. CRAIG & COMPANY LTD

CALEDONIA ENGINEERING WORKS

PAISLEY SCOTLAND

London Office 727 Salisbury House London Wall, E C 2.

Telephone MONARCH 4756

AFC/RP/3

Unique

"Newallastic" bolts and studs have qualities which are absolutely unique. They have been tested by every known device, and have been proved to be stronger and more resistant to fatigue than bolts or studs made by the usual method.

C. P. Newall & Co., Ltd.

POSSILPARK GLASGOW · N

Kindly mention this Journal when communicating with Advertisers